

CELLULAR PLASTICS
TECHNOLOGY

POLYMER CONFERENCE SERIES

WAYNE STATE UNIVERSITY

MAY 1-MAY 5, 1967

COLLEGE OF ENGINEERING

DIVISION OF URBAN EXTENSION

10214

CELLULAR PLASTICS TECHNOLOGY

May 1-5, 1967

Monday, May 1

8:15 A.M.

Introduction

8:30 A.M.

Lecture 1

"Catalysis of Urethane
Foams"

K. C. Frisch

Wyandotte Chemicals Corp.

29653

9:45 A.M.

Discussion

10:00 A.M.

Coffee Break

10:15 A.M.

Lecture 2

"The Role of Silicone
Surfactants in the
Stabilization of Urethane
Foams"

B. Kanner, Silicones Div.
Union Carbide Corp.

29654

11:30 A.M.

Discussion

11:45 A.M.

Lunch

1:00 P.M.

Lecture 3

"Spray Applied Rigid
Urethane Foam for Indust-
rial Insulation"

C. Hilado, Chemicals Div.
Union Carbide Corp.

29655

2:15 P.M.

Discussion

2:30 P.M.

Coffee Break

2:45 P.M.

Lecture 4

"Polyethylene Foam I-modified
~~Orientation~~ PE foam systems

C. J. Benning

W. R. Grace & Company

29656

4:00 P.M.

Discussion

4:15 P.M.

Panel Review

5:00 P.M.

Adjourn

7:00 P.M.

Informal Reception

Tuesday, May 2

Lecture 5

"The Formation and
Examination of Cells
in Expandable Poly-
styrene Foams"

A. R. Ingram

Koppers Co., Inc.

29657

Discussion

Coffee Break

Lecture 6

"Outgassing of Rigid
Urethane Foam"

E. Cuddihy

Jet Propulsion Lab

29658

Discussion

Lunch

Lecture 7

"Electrical Properties
of Rigid Urethane Foam"

J. Moacanin

Jet Propulsion Lab

29669

Discussion

Coffee Break

Lecture 8

"Testing of Cellular
Plastics"

W. Ashe

Wyandotte Chemicals
Corporation

Discussion

Panel Review

Adjourn

DTIC QUALITY INSPECTED 1

Plastic # 10214

Wednesday, May 3

Lecture 17

"Small Scale Evaluation of
Flammability Characteristics
of Cellular Plastics

C. Hilado, Chemicals Div.
Union Carbide Corp.

29659

Discussion

Coffee Break

Lecture 18

"Flammability Characteristics
of Cellular Plastics"

I. N. Einhorn
Wayne State University

29660

Discussion

Lunch

Lecture 19

"Polyethylene Foam ^{III Orientation in}
~~Mechanical Properties by~~ ^{Thermoplastic foams}
~~Rate of Expansion"~~

C. J. Benning
W. R. Grace & Company

29661

Discussion

Coffee Break

Lecture 20

"Rigid Cellular PVC"

F. J. Wherley
B. F. Goodrich Co.

29662

Discussion

Panel Review

Adjourn

Thursday, May 4

Lecture 11

"Styrene-Butadiene Foams"

R. L. Zimmerman
Dow Chemical Company

29663

Discussion

Coffee Break

Lecture 12

"The Production and Thermo-
forming of Polystyrene Foam
Sheet"

T. P. Martens
Sinclair-Koppers Co.

29664

Discussion

Lunch

Lecture 13

"Cellular Plastics in
Packaging Applications"

J. Winne
Westinghouse Electric Corp.

29665

Discussion

Coffee Break

Lecture 14

"Chemical and Mechanical Factors
Affecting One-Shot Rigid Foams"

M. Kaplan, Industrial Chem. Div.
Allied Chemical Corporation

29666

Discussion

Panel Review

Adjourn

Cocktail Party (6:00 P.M.)
followed by Class Banquet

Friday, May 5

Lecture 15

"Microwave Curing of Cellular
Plastics"

W. J. Hoskin

Elliott Electronic Tubes, Ltd.

29667

Discussion

Coffee Break

Lecture 18

"Economics and Markets of
Cellular Plastics"

R. Siren

Mobay Chemical Company

Discussion

Adjourn

Lecture
16

"Chemically crosslinked polyethylene foams;"
by Yoshio Kadowaki

10 214-16

29668

10214-01

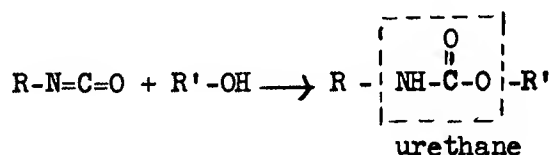
Catalysis in Polyurethane Foams

K. C. Frisch and S. L. Reegen^{id}
Wyandotte Chemicals Corporation
Wyandotte, Michigan 48192

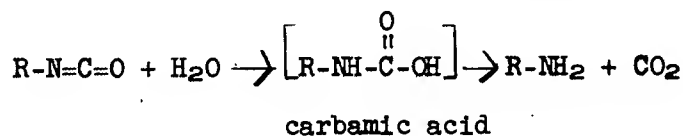
Catalysis plays a vital role in the production of urethane foams because it not only affects the rates of the chemical reactions responsible for foam formation but it also affects the ultimate properties of the resulting foams.

Urethane foam generation is the result of a series of rather complex reactions leading to the formation of linkages other than the urethane group although the resulting polymer is referred to simply as a "urethane." The basic reactions during foam formation are listed below, representing the materials in the monofunctional form for simplicity sake.

The two most important reactions in the manufacture of flexible urethane foams are the reaction between isocyanate and hydroxyl-containing compounds (polyether or polyester polyols) and the reaction between isocyanate and water. The former is the basic reaction for the formation of urethane groups and can be considered as the chain propagating reaction:

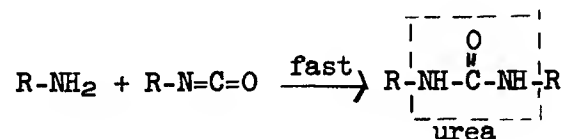


The second reaction is responsible for the foaming of the urethane polymer by the liberation of carbon dioxide with simultaneous formation of substituted urea groups. The first step in this reaction is the formation of the unstable carbamic acid which decomposes to form an amine and carbon dioxide:

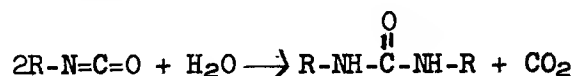


The amine immediately reacts with additional isocyanate to form a substituted

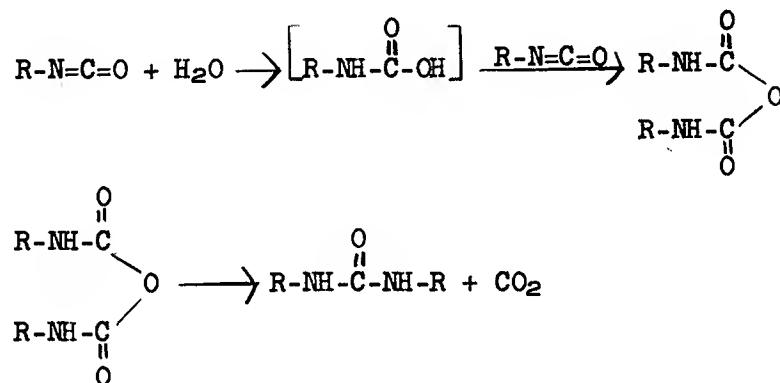
urea as follows:



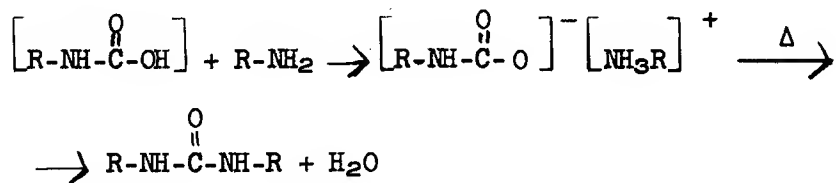
The overall reaction can be represented as:



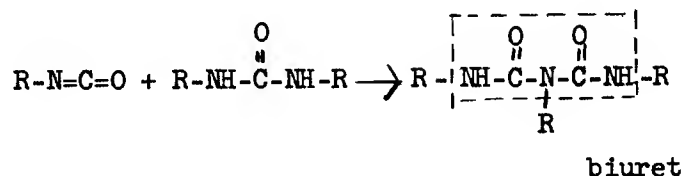
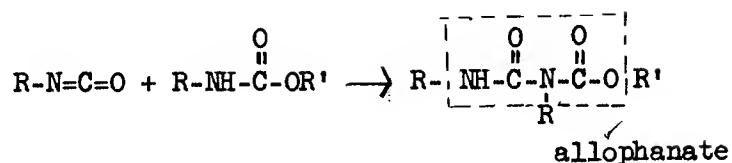
An alternate mechanism provides for formation of a carbamic acid anhydride, followed by decomposition to a substituted urea and carbon dioxide:



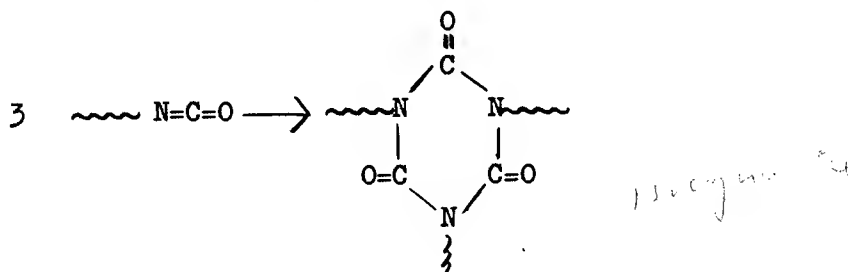
Still another reaction which may occur to some extent is the formation of the amine salt of carbamic acid which decomposes under the influence of heat to yield water and urea:



Other reactions which lead to branching and crosslinking in urethane foams are the formation of allophanate and biuret linkages:



Still another crosslinking reaction is trimerization, leading to the formation of isocyanurate rings which are hydrolytically and thermally very stable.



Since most of the above reactions are too slow for the commercial manufacture of urethane foams, catalysts are employed whose functions are not only to bring about faster rates of reaction but also to establish a proper balance between the chain propagation reaction (mainly the hydroxyl-isocyanate reaction) and the foaming reaction (isocyanate-water reaction in the case of flexible foams). A balance has to be established between gas formation and polymer growth in order to entrap the gas (CO₂) efficiently and to develop sufficient strength in the cell walls at the end of the foaming reaction (evolution of gas) to maintain their structure without collapse or shrinkage.

Another important function of catalysts in foam reactions is to bring about completion of the reactions, resulting in an adequate "cure" of the foam. Completion of cure results in maximum strength properties, minimum compression set and maximum chemical and weathering resistance. Progress of cure can also

be determined by means of differential thermal analysis (DTA), infrared absorption and Vicat softening point data (1,2).

The catalysts most commonly employed are tertiary amines and metal catalysts, especially tin catalysts. Tertiary amines are catalysts for both the isocyanate-hydroxyl as well as the isocyanate-water reaction. The efficiency of tertiary amine catalysts depends upon their chemical structure. It generally increases as the basicity of the amine increases and the steric shielding of the amino nitrogen decreases (3,4). Table I (5) shows the importance of steric factors in the catalytic activity of tertiary amines. Some of the most commonly used tertiary amine catalysts are triethylene diamine ("Dabco," Houdry Process & Chem. Co.), N-alkyl morpholines, N,N,N',N'-tetramethylethylene diamine, N,N,N',N'-tetramethyl-1,3-butanediamine, N,N'-substituted piperazines, and dialkyl-alkanolamines.

Organotin compounds are extremely effective catalysts for the isocyanate-hydroxyl reaction. They include stannous octoate, stannous oleate, dibutyltin dilaurate and dibutyltin di-2-ethylhexoate. They are often used in conjunction with small concentrations of antioxidants such as t-butyl catechol, resorcinol, tartaric acid, etc.

It is common practice to use combinations of tertiary amines and tin catalysts in the production of flexible foams and to some extent in rigid foams requiring a "hot" catalyst system such as for spray foams or for the manufacture of structural panels. In other cases rigid foams are made employing tertiary amine catalysts either singly or in combination (e.g. N,N,N',N'-tetramethylethylenediamine and dimethylethanolamine).

Table II shows the relative order of activity of various catalysts and

TABLE I
RELATIVE CATALYTIC ACTIVITY OF AMINE CATALYSTS

Chemical Name of Amine Catalyst	Chemical Formula	pK _a	Relative Catalytic Activity
1,4-Diazabicyclo(2,2,2)- octane		5.4	23.9
N,N-Diethylcyclohexyl- amine		10.0	0.7
N-Methyl-morpholine		7.4	1.0
N,N,N',N'-Tetramethyl- methane diamine	(CH ₃) ₂ NCH ₂ N(CH ₃) ₂	10.6	0.085

TABLE II

RELATIVE REACTIVITY OF CATALYSTS IN ISOCYANATE-HYDROXYL REACTION

Catalyst	Concentration %	Order of Activity
Uncatalyzed	-	1
TMEDA	0.1	56
DABCO	0.1	130
TMEDA	0.5	160
DBTDL	0.1	210
DABCO	0.2	260
DABCO	0.3	330
SnOct	0.1	540
DBTDL	0.5	670
DBTDL + TMEDA	0.1 + 0.2	700
SnOct + TMEDA	0.1 + 0.2	1000
DBTDL + DABCO	0.1 + 0.2	1000
SnOct + TMEDA	0.1 + 0.5	1410
SnOct + DABCO	0.1 + 0.5	1510
SnOct	0.3	3500
SnOct + DABCO	0.3 + 0.3	4250

TMEDA = Tetramethylbutanediamine
DABCO = 1,4-Diaza(2,2,2)bicyclooctane

DBTDL = Dibutyltin dilaurate
SnOct = Stannous octoate

catalyst combinations in a model isocyanate-hydroxyl reaction (6,7). It also points out clearly the synergistic effect between tin catalysts and tertiary amines. It is of interest to note that a synergistic effect has also been observed with two tertiary amine catalysts, e.g. tetramethylbutanediamine and triethylamine (7). This is probably due to a combination of two different factors--relative lack of steric hindrance and effect of relatively strong basicity.

The relative order of activity of some catalysts for the water-isocyanate reaction is seen in Table III (8).

The catalyst balance in a foam is often measured by means of porosity or "breathability" tests. Porosity is measured by determining the flow rate of air at a given pressure drop through a foam specimen; breathability measures the pressure drop across the test specimen at a certain flow rate of air. When the gelation reaction becomes more predominant, the number of closed cell-faces becomes greater and the porosity decreases.

The processability of different foam systems can often be evaluated by plotting the porosity against the catalyst concentration (by varying catalyst concentration over a range which still produces good foam). The shape of the resulting curve as well as the catalyst concentration range between "split" and "tight" foam give an indication of the catalyst (tin) operating range. If the tin catalyst concentration is decreased excessively (below the lower end of the range) "splits" occur in the foam, while excessive increase of the tin catalyst concentration (above the upper end of the range) results in "tight" foams (an arbitrary level of porosity to denote the upper limit of the catalyst concentration).

TABLE III

RELATIVE REACTIVITY OF CATALYSTS IN ISOCYANATE-WATER REACTION
0.1 pts. Catalyst per 100 pts. Resin

Catalyst	Order of Activity
Stannous octoate	1.0
N-Ethyl morpholine	1.1
Dibutyltin dilaurate	1.3
Triethylamine	1.5
N,N,N',N'-Tetramethyl-1,3-butane diamine	1.6
1,4-Diaza(2,2,2)bicyclooctane (DABCO)	2.7

While the nature and the concentration of the polyol, isocyanate, and blowing agent have the greatest effect on the foam properties, catalysts also influence foam properties. These effects are summarized in Table IV (9).

The effect of catalysts on foam reactions can be determined quantitatively by determining the reaction kinetics, i.e. the rates of reaction of a particular system. This is usually being done by measuring the disappearance of isocyanate in the reaction with active hydrogen-containing compounds. Usually model compounds are used in these studies and solvents are employed which affect the rates of reaction. In an actual foaming system the situation is complicated by the fact that a number of simultaneous reactions may occur which are exothermic, thus changing the rates of reaction with temperature rise as the reaction proceeds. Nevertheless, the kinetic studies with model reactions are significant as they shed considerable light on the relative rates of reaction of isocyanates with various active hydrogen compounds and provide an insight into the mechanism of catalysis in isocyanate reactions.

TABLE IV

ONE-SHOT POLYETHER URETHANE FLEXIBLE FOAMS
EFFECT OF CATALYST CONCENTRATION

SnOct = 0.25-0.35 phr Amine <0.1 phr

Property	Usual Response Caused by Increasing Concentration of:	
	Tin	Amine
Rise Time	Decreases	Decreases
Porosity	Decreases	Increases
Density	Decreases	Increases slightly
ILD (<i>Initial Tensile Load Deflection</i>)	Increases slightly	Decreases
Tensile strength	Increases	Decreases
Elongation	Increases	-
Resilience	Decreases slightly	Increases slightly
Compression Set	Increases	Increases
Flex Fatigue	Increases slightly	Decreases slightly

In the course of a study of the kinetics of alcohol and polyol-isocyanate reactions using metal catalysts, the interesting observation was made that the relative rates of the reactions of model hydroxyl compounds with isocyanates (10,11,12) were reversed when a lead catalyst was used instead of a tin catalyst. Specifically, when employing methoxy-propanols as the model hydroxyl compounds, the reaction rates observed with dibutyltin dilaurate catalyst in toluene solution at 30°C. are shown in Figure 1. As could be expected, both the position of the methoxy group and the nature of the hydroxyl group had a pronounced effect on the reaction rates. Using dibutyltin dilaurate, 3-methoxy-1-propanol exhibited the fastest rate, followed by 2-methoxy-1-propanol and 1-methoxy-2-propanol. However, when employing lead naphthenate as catalyst, 2-methoxy-1-propanol had the fastest rate, followed by 1-methoxy-2-propanol with 3-methoxy-1-propanol exhibiting the slowest rate (see Figure 2). The same trend in reaction rates was observed when either cellosolve acetate or toluene was used as solvent although the rates were considerably slower in the case of cellosolve acetate (Figures 3 and 4). This is as would be expected in the case of a polar solvent involving presumably interaction (complex formation) between the polar solvent and the alcohol.

These apparent variations in catalytic activity have led to further attempts to elucidate the mechanism involved, including a search for evidence of complex formation by the interaction of these catalysts with alcohol and isocyanate.

Infrared Spectroscopy

Smith (13) has reported evidence, based on infrared spectra, for the presence of a ternary complex as the reactive intermediate in the alcohol-isocyanate reaction catalyzed by metal salts, such as stannous 2-ethylhexoate. He

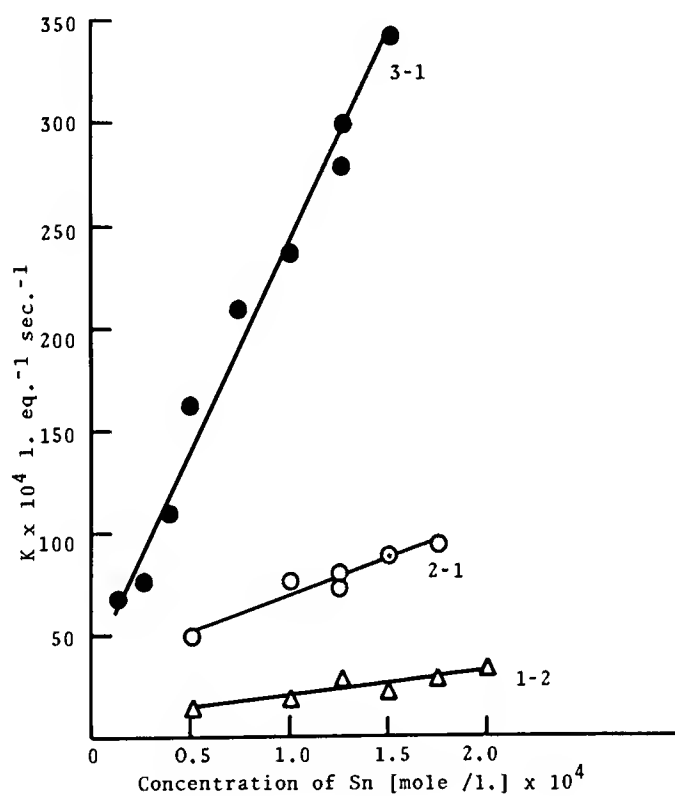


Figure 1

Effect of Sn Concentration on Second Order Rate Constant.

Reaction of Phenyl Isocyanate with 1-Methoxy-2-propanol (1-2)

2-Methoxy-1-propanol (2-1)

3-Methoxy-1-propanol (3-1)

In Toluene at 30°C .

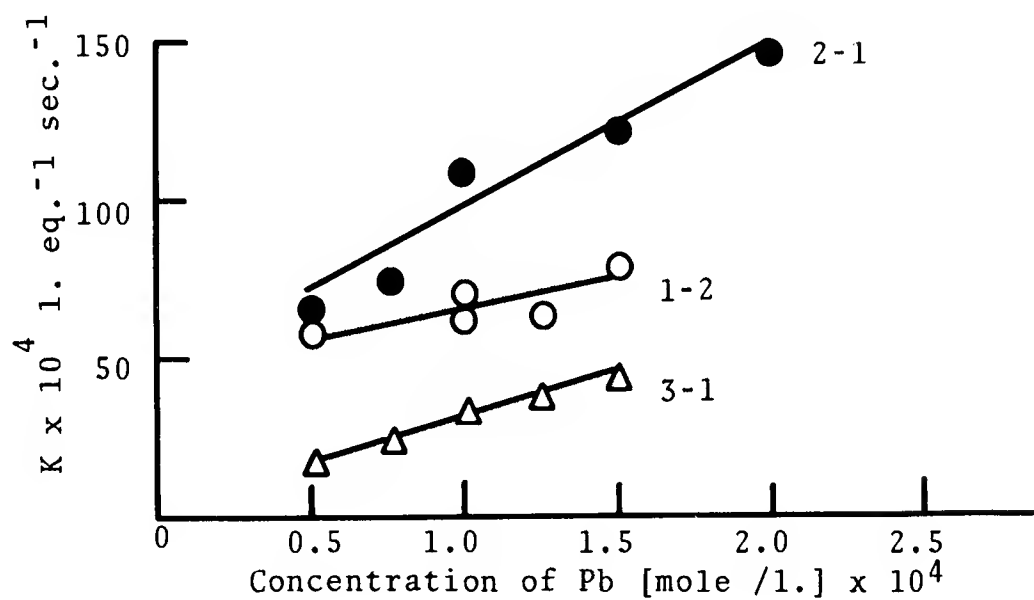


Figure 2

Effect of Pb Concentration on Second Order Rate Constant.

Reaction of Phenyl Isocyanate with 1-Methoxy-2-propanol (1-2)

2-Methoxy-1-propanol (2-1)

3-Methoxy-1-propanol (3-1)

In Toluene at 30°C .

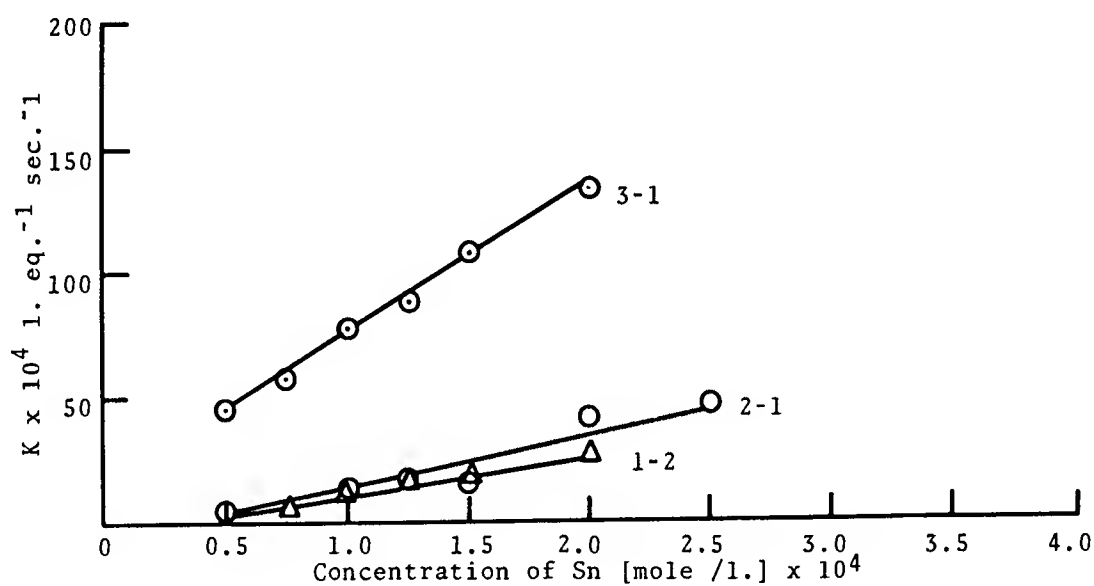


Figure 3

Effect of Sn Concentration on Second Order Rate Constant.

Reaction of Phenyl Isocyanate with 1-Methoxy-2-propanol (1-2)
 2-Methoxy-1-propanol (2-1)
 3-Methoxy-1-propanol (3-1)

In Cellosolve acetate at 30°C .

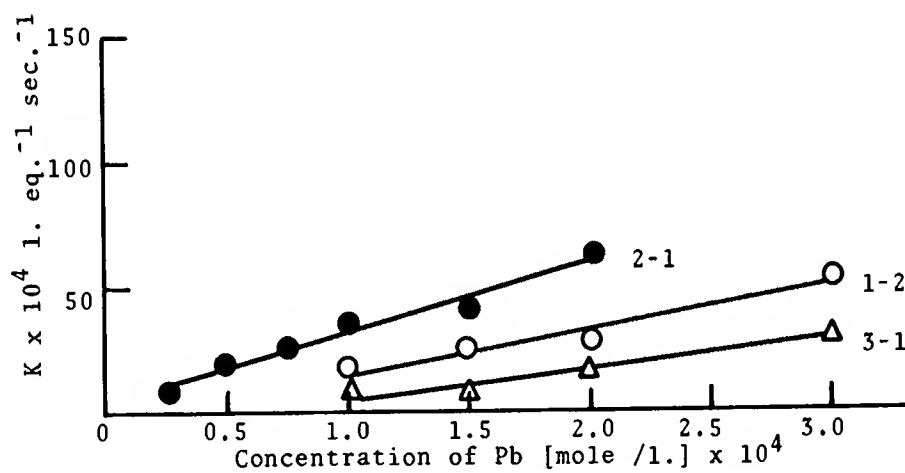


Figure 4

Effect of Pb Concentration on Second Order Rate Constant.

Reaction of Phenyl Isocyanate with 1-Methoxy-2-propanol (1-2)

2-Methoxy-1-propanol (2-1)

3-Methoxy-1-propanol (3-1)

In Cellosolve acetate at 30°C.

attributed shifts in absorption bands to the formation of reactant-catalyst complexes. In our study, mixtures of 10-20% dibutyltin dilaurate or stannous 2-ethylhexoate in 1-methoxy-2-propanol or phenyl isocyanate were examined. No significant evidence for band shifts or intensity changes could be observed. Mixtures of reactant-catalysts in 1:1 ratio gave evidence of a slight shift in the -OH band to a lower frequency. This can be attributed to a change in the hydrogen bonding character of the system but does not provide proof for complex formation.

Pestemer and Lauerer (14) proposed that new absorption bands which appeared in their IR spectra of catalyst-phenyl isocyanate mixtures were due to the formation of an addition complex; they did not show evidence for the band shifts reported by Smith. Using amine or organometallic catalysts, they observed decrease or disappearance of -NCO absorption in isocyanate-catalyst mixtures. Their procedures were followed closely in our study, but no evidence of complex formation was observed. Indications were obtained only of a reaction between trace moisture and phenyl isocyanate. No measurable decrease in -NCO absorption, in the presence of excess catalyst, could be detected. More recent work by Farkas and Strohm (15) using this method was in agreement with our data; they could find no evidence of catalyst-isocyanate complexing when the samples were completely devoid of moisture.

These results point out limitations in applying infrared spectroscopy to the detection of alcohol or isocyanate complexing with metallic catalysts. At normal catalyst levels, the concentration of any complex intermediates is below that required for detection by infrared. When the catalyst concentration is increased to a reactant level, spectral changes can occur that are un-

related to complex formation.

U.V. Spectroscopy

Examination of UV spectra for phenyl isocyanate and for mixtures of phenyl isocyanate with tertiary amines, tri-n-propylamine and triethylamine, in a manner similar to that reported by Pestemer and Lauerer (14), and with organo-metallic catalysts (lead naphthenate and stannous octoate) resulted in no detection of catalyst-isocyanate complexes. Absorption maxima for the benzenoid chromophore in the dry cyclohexane solution were unaffected by the presence of the catalyst compounds, even when approximately equivalent amounts of isocyanate and catalyst were employed. Combinations of amine and organometallic catalysts also had no effect on the phenyl isocyanate absorption maximum. The UV spectrum for a non-aromatic isocyanate, hexamethylene diisocyanate, was also investigated, but exhibited no distinct absorption in the 220 mμ. - 375 mμ. UV range for the N=C=O chromophore.

Nucleomagnetic Resonance (NMR)

Little work has been reported utilizing the NMR technique for the study of urethane reactions. Sumi et al (16) have reported the spectra of a series of urethanes to identify the nitrogen-containing linkages, but the technique has not been previously reported for the study of the mechanism of the reaction between alcohols and isocyanates, in the presence of catalyst, to form urethanes.

NMR spectra were recorded on a Varian Model DP-60 and a Varian Model A-60 spectrometer at ambient temperatures. The chemical shift was expressed in terms of the parameter in ppm, using tetramethylsilane (TMS) or cyclohexane as the internal reference. A study of the dibutyltin dilaurate:1-methoxy-2-propanol system was started by examination of the spectra of each of the two

components in carbon tetrachloride solution (12). Due to the complexity of the spectrum, a complete assignment for the dibutyltin dilaurate peaks was not possible; they all occurred in a very narrow region. The assignments for the peaks in 1-methoxy-2-propanol are given in Table V as well as the effect of concentration on their positions. It is apparent that only the peak associated with the -OH proton exhibits significant downfield shifts with increasing alcohol concentration, indicative of increased hydrogen bonding.

On mixing the two compounds it can be seen (Figure 5) that the peak associated with the -OH group shifted downfield considerably with increasing concentration of Sn, which may be readily interpreted on the basis of complex formation between the catalyst and the alcohol, resulting in electron withdrawal from the hydroxyl group. The shifts measured were downfield from tetramethylsilane which was used as an internal standard. It is evident from Figure 5 that a 1:1 complex is formed; a sharp decrease in slope of the plot of chemical shift vs. catalyst concentration is obtained beyond the addition of equimolar concentrations of Sn to the alcohol. The continued increase in chemical shift beyond that concentration may be due to the existence of additional complexes.

A study of the lead naphthenate:1-methoxy-2-propanol system in carbon tetrachloride and cyclohexane solution was also carried out (12). Figure 6 clearly shows the formation of a stable complex; the peak associated with the -OH group shifted downfield with increasing concentration of Pb. The composition of the complex was not determined, although it can be seen that the ratio of Pb:alcohol was at least 1:1.

The data resulting from the triethylamine:1-methoxy-2-propanol system in

TABLE V

CONCENTRATION DEPENDENCE OF THE NMR SPECTRUM OF 1-METHOXY-2-PROPANOL

Conc. of Alcohol (m/l)	$\text{CH}_3 - \overset{\text{OH}}{\underset{ }{\text{CH}}} - \text{CH}_2 - \text{OCH}_3$	$\text{CA}_3 - \overset{\text{O-D}}{\underset{ }{\text{CB}}} - \text{CE}_2 - \text{OCF}_3$	NMR Shift			
			δ ppm			
	A	B	D	E	F	
0.54	-	-	2.56	-	-	
0.62	1.00 1.13	-	2.75	3.12 3.19 3.23	3.36	
1.03	1.02 1.14	-	2.93	3.15 3.21 3.25 3.28	3.38	
3.10	0.99 1.09	-	3.52	3.19 3.22 3.30	3.37	

letters identify protons below

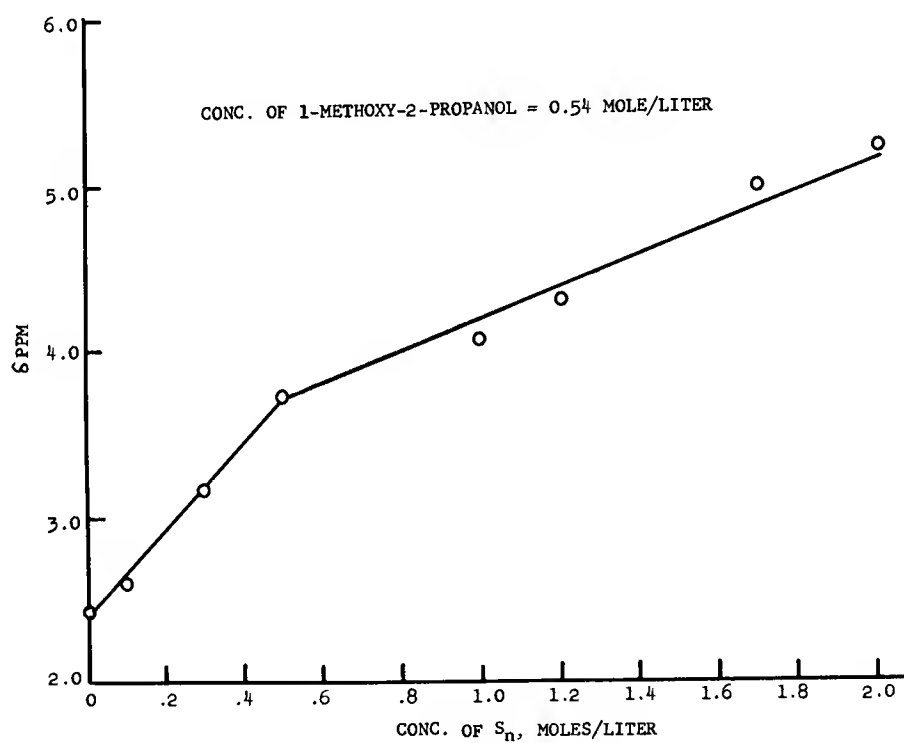


Figure 5

Effect of Sn Concentration on Shift of -OH Proton by NMR

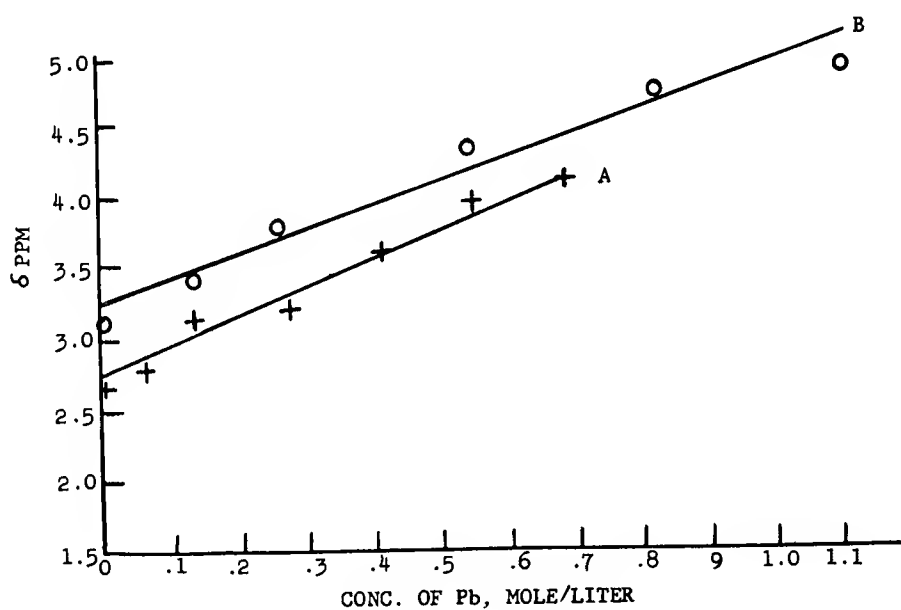


Figure 6

Concentration dependence of the OH NMR resonance of 1-methoxy-2-propanol on lead naphthenate concentrations:

- (A) TMS used as internal standard, CCl_4 solution, concentration of ROH = 0.53 mole/l.
- (B) Cyclohexane used as solvent and internal standard corrected to TMS by the addition of 86 cps. concentration of ROH = 0.56 mole/l.

cyclohexane solution are shown in Figure 7. The downfield shift of the -OH resonance with increasing concentration of catalyst is evidence of association between the amine catalyst and alcohol. This shift is significantly less than that caused by either of the two metal catalysts. It may be assumed that the hydrogen-bonding type of interaction resulting from the addition of amine to the alcohol is of a lower energy than the oxygen-metal bond in the complex resulting from the addition of either Sn or Pb to the alcohol.

The effect of catalyst combinations on complex formation was also investigated, using solvent-free mixtures of catalyst and alcohol (12). The shift of the -OH peak was determined on the addition of triethylamine, dibutyltin dilaurate and mixtures of the two catalysts. The data in Table VI show the shift to be greater for the mixture of the two catalysts than for either catalyst alone, indicating that both hydrogen-bonds and oxygen-metal bonds are formed. The direction of the shifts was opposite to that expected from dilution of the -OH proton. The increased shift appears to correlate with the synergistic effect noted when preparing urethanes with a mixture of these two catalysts.

Isocyanate-Catalyst Complexes by NMR

Efforts were also made to detect complex formation in mixtures of phenyl isocyanate and catalyst. As can be seen in Table VII no significant shifts occurred by the interaction with triethylamine; this is true for protons on the phenyl group of the isocyanate (two prominent peaks were obtained in the phenyl region) or on the methyl and methylene groups of the amine. Table shows that no shifts occurred (for protons on the phenyl group) on the addition of dibutyltin dilaurate to phenyl isocyanate. These data indicate that there are no interactions between the isocyanate group and these catalysts that are

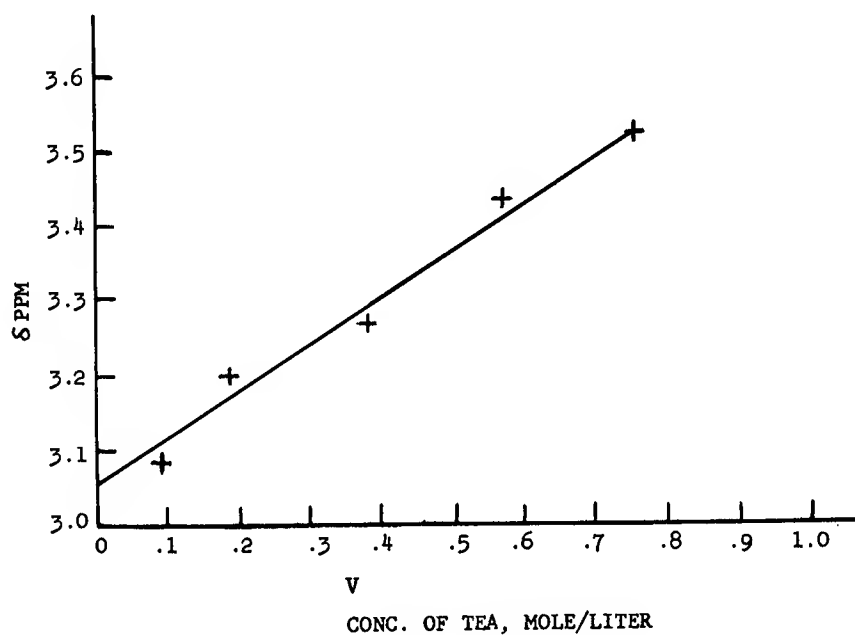


Figure 7

Concentration dependence of the OH proton of 1-methoxy-2-propanol on triethylamine concentration. Cyclohexane was used as solvent and internal standard, corrected to TMS by the addition of 86 cps. Concentration of ROH = 0.50 mole/l.

TABLE VI

EFFECT OF TRIETHYLAMINE-DIBUTYLITIN DIIAURATE MIXTURE ON CHEMICAL SHIFT
OF OH PROTON IN 1-METHOXY-2-PROPANOL

Mole Ratio of Alcohol/TEA/DBTDL	δ ppm (a)
5/0/0	4.22
5/1/0	4.44
5/0/1	4.47
10/1/1	4.94

(a) ppm shift based on TMS

TABLE VII
THE EFFECT OF MIXTURES OF TRIETHYLAMINE AND PHENYL ISOCYANATE ON NMR SPECTRA

Conc. of $N(C_2H_5)_3$ moles/liter (a)	CH_3 (b)	$\frac{\delta \text{ ppm}}{CH_2}$	Phenyl ₁	Phenyl ₂
0	-	-	6.98	7.07
.095	0.95	2.41	7.00	7.09
.189	0.96	2.44	7.01	7.09
.379	0.97	2.45	7.02	7.11
.568	0.95	2.39	7.01	7.11
.758	0.95	2.44	7.01	7.10

(a) Cyclohexane was used as solvent and internal standard, corrected to TMS by the addition of 86 cps (phenyl isocyanate = 0.54M).

(b) The CH_3 resonance is upfield from TMS; all other lines are downfield.

measurable by NMR spectroscopy.

Since NMR data provided only evidence for alcohol-catalyst complexes but not isocyanate-catalyst complexes, other methods were studied to produce experimental evidence for the latter. The two methods which were successfully employed for this investigation were enthalpimetry and determination of molecular weights by means of freezing point depression.

Enthalpimetry

Enthalpimetry is based on the principle that the change in temperature in an adiabatic system represents the extent of reaction in a well-defined process. The use of thermistors in a Wheatstone Bridge makes possible the detection of small temperature changes in reactions involving submillimolar samples in dilute solutions. Thus, a reaction may be readily followed by detecting the temperature change as a function of time.

The enthalpimetric titration apparatus, shown in Figure 8, consisted of two major components: an adiabatic reaction cell, and a detection circuit. The cell was a 50 ml., 3-necked round bottom flask imbedded in rigid polyurethane foam. The foam provided the insulation necessary for adiabatic conditions. The solutions were stirred by means of a variable speed motor with the stirrer entering the reaction cell through the center neck of the flask. The cell was sealed at this point by means of a ball and socket joint. The male union was attached to the shaft of the stirrer by means of rubber tubing. The female joint was connected to the reaction cell by means of a standard ground glass joint.

The detection circuit consisted of a thermistor bridge, the output of which was used to drive the pen of a Sargent Recorder Model SR. The thermistor was

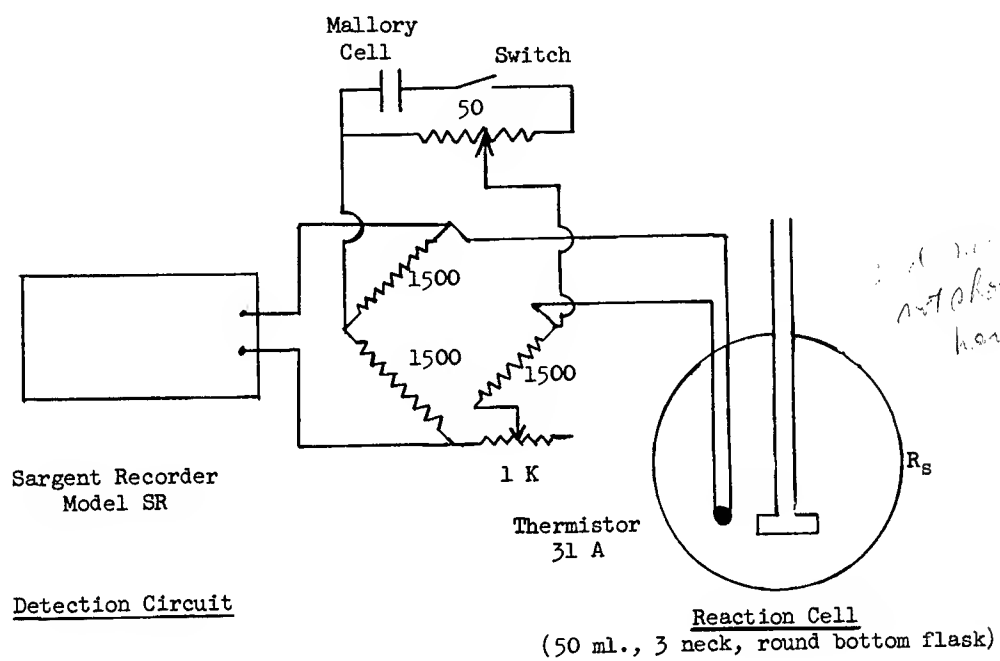


Figure 8

Enthalpimetric Titration

immersed in the solution in the cell through a silicone rubber seal in one neck of the cell.

The third neck of the cell was closed by means of a silicone rubber puncture seal. Aliquots of reagent were introduced into the cell by means of Hamilton micro syringes through the seal in the third neck of the flask. During injection of the reagent the tip of the needle was immersed in the solution so that no reagent would be lost by drops adhering to the needle.

Method

Standard solutions of phenyl isocyanate, 1-methoxy-2-propanol, dibutyltin dilaurate, stannous octoate, and lead naphthenate were prepared using water-free benzene as the solvent. Portions of the reagents were weighed directly into 50 ml. tared volumetric flasks. The solutions were made up to volume with the benzene. The resulting solutions were approximately 0.08 molar.

An aliquot of the catalyst solution was added to 15 ml. of benzene in the reaction cell. This solution was stirred continuously and allowed to come to thermal equilibrium. Increments of the phenyl isocyanate or 1-methoxy-2-propanol solutions were added by means of a syringe and the deflection of the recorder observed. The weight of solution added was determined by weighing the syringe before and after addition of the reagent.

The end point of the titration was determined by plotting recorder deflection versus the weight of reagent added and was indicated by a change in slope with further addition of reagent. The stoichiometry of the complex formed was calculated from the molar quantities of catalyst and reagent in the cell at the inflection points of the resulting plots.

A typical plot of recorder response and volume of titrant is shown in Figure 9. The plot was obtained by titrating 5 ml. of 0.0472 molar 1-methoxy-2-propanol with 0.0464 molar dibutyltin dilaurate. The resulting inflection point corresponds to 4.76 ml. of dibutyltin dilaurate solution; i.e. the catalyst forms a 1:1 complex with 1-methoxy-2-propanol.

The data obtained are shown in Table VIII. In the case of mixtures of DBTDL and 1-methoxy-2-propanol (where the catalyst solution was titrated into the alcohol solution) evidence was obtained for a 1:1 complex. A break in the ΔH_f vs. concentration plot was obtained only at that one concentration. In the case of mixtures of phenyl isocyanate and DBTDL (where the catalyst solution was titrated into the isocyanate solution) indications of two types of complexes were obtained; both 1:2 and 1:1 catalyst:isocyanate complexes were formed.

The use of stannous octoate in combination with 1-methoxy-2-propanol (titrating the alcohol solution into the catalyst solution) resulted in evidence for the formation of five types of complexes; the use of lead naphthenate as the catalyst appeared to produce three types of complexes. However, only the 1:1 complex was detected in mixtures of lead naphthenate and phenyl isocyanate.

Cryoscopy

The molecular weight of complexes were determined in benzene solution from the freezing point depression of the benzene:

$$M = \frac{1,000 K_f g}{G \Delta T_f}$$

where M = molecular wt. of solute
 ΔT_f = observed depression of freezing point of benzene
 g = weight of solute in grams
 G = weight of benzene in grams
 K_f = freezing point constant (5.12 for benzene)

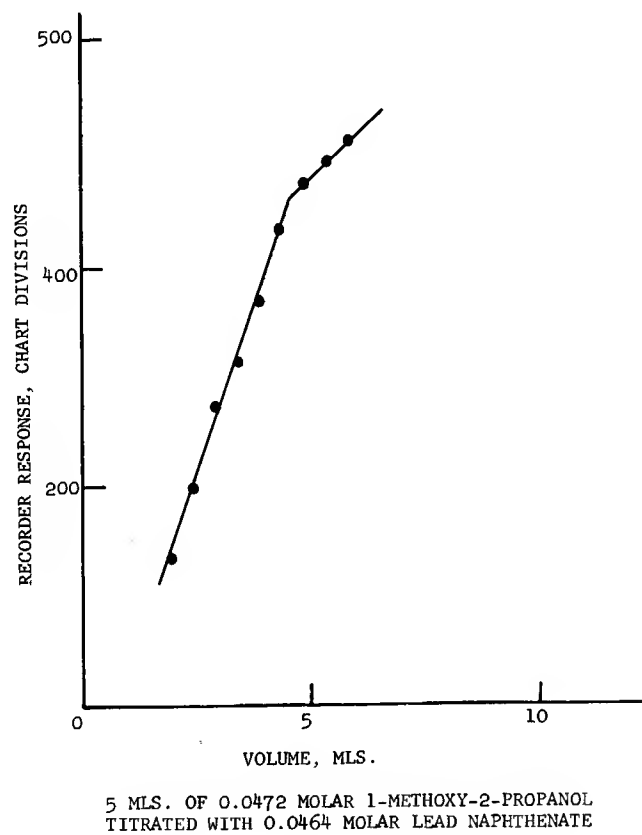


Figure 9

Typical Plot of Recorder Response During Enthalpimetric Titration

TABLE VIII

STOICHIOMETRY OF COMPLEXES AS DETERMINED BY ENTHALPIMETRY

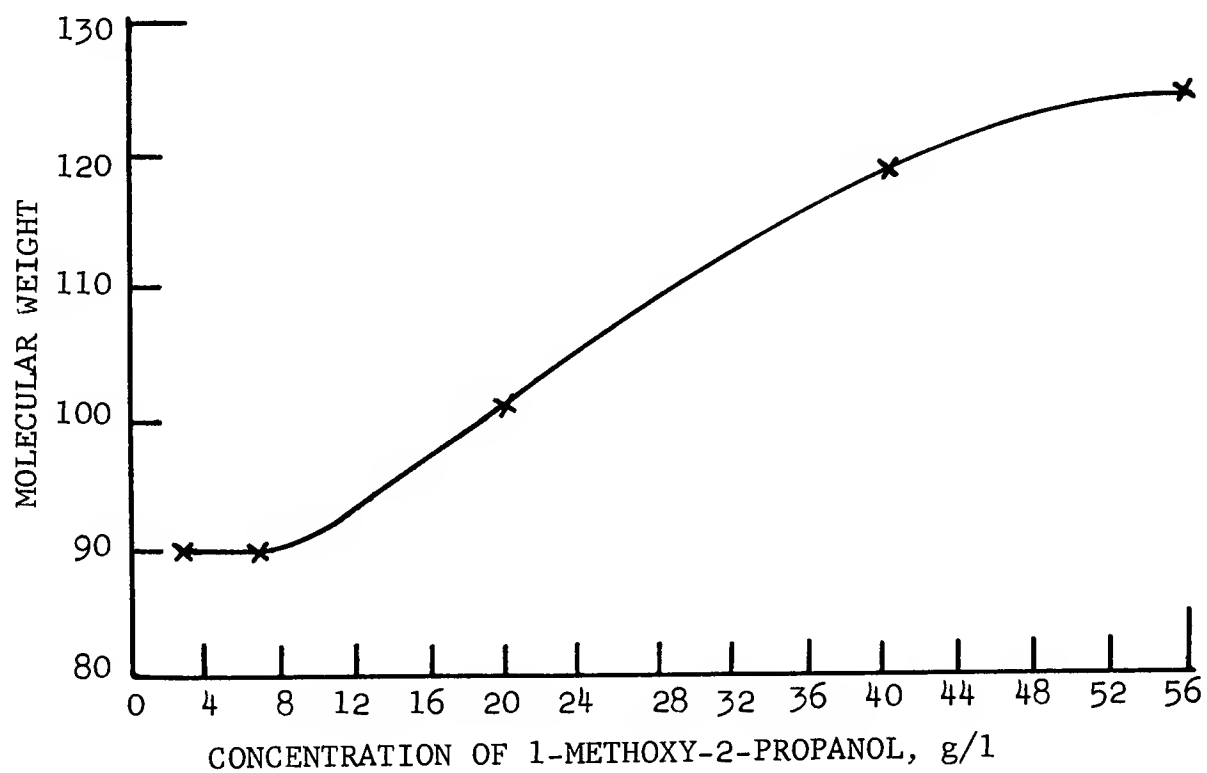
$\frac{\text{Catalyst}}{(A)}$	$\frac{\text{Reactant}}{(B)}$	Stoichiometry of Complexes
Dibutyltin dilaurate	1-Methoxy-2-Propanol	AB
Dibutyltin dilaurate	Phenyl Isocyanate	AB ₂ AB
Stannous octoate	1-Methoxy-2-Propanol	A ₂ B A ₂ B ₃ A ₅ B ₇ A ₄ B ₇ AB ₂
Lead Naphthenate	1-Methoxy-2-Propanol	A ₂ B ₃ AB AB ₂
Lead Naphthenate	Phenyl Isocyanate	AB

Complex formation was detected by determination of molecular weights of mixtures of alcohols or isocyanates and catalysts. The formation of complexes should result in significantly higher molecular weights than would result from no interaction between reactants and catalysts.

In Figure 10 the molecular weight of 1-methoxy-2-propanol is shown to be dependent on its concentration in benzene; hydrogen bonding between the alcohol groups appears to play an important role at concentrations higher than 6.5 g/l, resulting in significantly higher molecular weights than the theoretical value of 90.

In Table IX the molecular weight of dibutyltin dilaurate (DBTDL), as determined by the freezing point depression of benzene, is shown to change very little with increasing concentration of DBTDL. Thus, only a 2.5% increase in M.W. resulted when the concentration of DBTDL was increased from 81 to 242 g/l. These molecular weights were all slightly under the theoretical value of 599.

In Table X the data resulting from mixtures of 1-methoxy-2-propanol and DBTDL are shown. In these determinations, the concentrations of alcohol were maintained constant at 45 g/l, while the concentration of DBTDL was increased in succeeding measurements. The molecular weights that were experimentally determined can be compared with the theoretical values calculated on the basis of (a) no complex formation, and (b) 100% complex formation. It should be noted that a value of 119 was used in calculations for the M. W. of 1-methoxy-2-propanol, as determined previously for this concentration, and values of 561 and 575 were used for the M. W. of the DBTDL. It is apparent that the molecular weights obtained were, in each case, higher than those calculated for no complex formation and lower than those calculated for 100% complex formation.



avg 117

Figure 10

Molecular Weight of 1-Methoxy-2-Propanol by Freezing Point Depression
of Benzene

TABLE IX

MOLECULAR WEIGHT OF DIBUTYLtin DILAURATE BY FREEZING POINT DEPRESSION OF BENZENE

Concentration DBTDL in Benzene, g/l	$\frac{\text{M. W.}}{(\text{Theoretical} = 599)}$
80.6	561
160.2	575
241.5	575

TABLE X

COMPLEX FORMATION IN MIXTURES OF
1-METHOXY-2-PROPANOL AND DIBUTYLIN DITHIOATE
BY FREEZING POINT DEPRESSION OF BENZENE

CONC. OF 1-METHOXY- 2-PROPANOL, g/l	CONC. OF DBTDL, g/l	CALCULATED M.W.		EXPERIMENTAL M.W. (c)	CATALYST IN COM- PLEX, % $\frac{c-a}{b-a} \times 100$
		NO COMPLEX (a)	100% COMPLEX (b)		
45.0	0	90	-	119	-
45.0	50.5 ¹⁾	204	226	213	41
45.0	178.3 ²⁾	324	588	352	11
45.0	247.3 ²⁾	361	680	390	9

1) M.W. of DBTDL = 561

2) M.W. of DBTDL = 575

The experimentally determined molecular weights were significantly higher than the calculated values for no complex formation and are strong evidence of alcohol-Sn complexing in each case. When calculations were made of the concentration of catalyst tied up in complex formation $\frac{c-a}{b-a} \times 100$, one can observe that it decreases with increasing DBTDL content in solution.

It should be noted that these determinations of complex formation were made at a concentration of 1-methoxy-2-propanol (45 g/l) at which there was significant hydrogen-bonding (Figure 11). Determinations at alcohol concentration at which no hydrogen-bonding had been detected (6 g/l) resulted in no evidence of complex formation with DBTDL.

Similar measurements were made on mixtures of 1-methoxy-2-propanol and triethylamine (TEA). As shown in Table XI, the molecular weight of TEA changed very little with increasing concentration (9.1 to 52.5 g/l). In Table XII the data resulting from mixtures of 1-methoxy-2-propanol and TEA are shown. In these determinations, the concentrations of alcohol were maintained constant at 54.8 g/l, while the concentration of TEA was increased in succeeding measurements. A value of 124.5, as determined previously for this concentration, was used in these calculations as the molecular weight of 1-methoxy-2-propanol, and values of 99 and 102 were used as molecular weights of the catalyst, TEA. These molecular weights were significantly higher than the calculated values for no complex formation, and appear to be evidence of alcohol-amine complexing in each case. It can also be seen that the concentration of catalyst tied up in the complexes seems to decrease in increasing TEA content in solution.

These molecular weight determinations appear to be significant evidence of

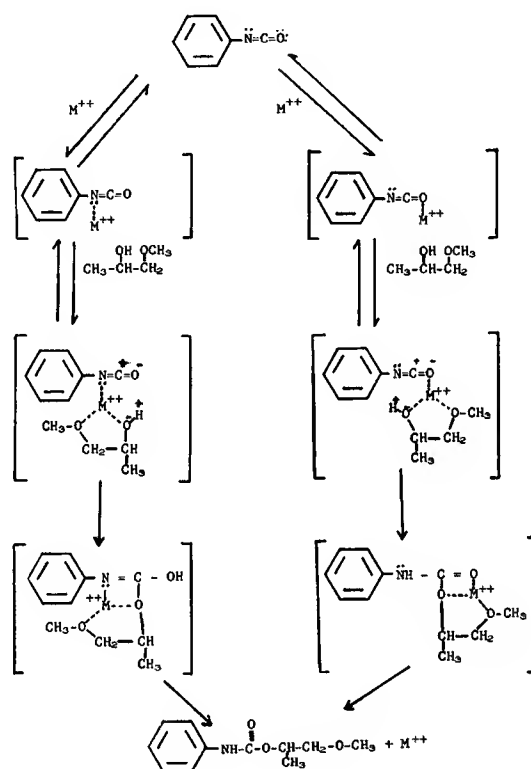


Figure 11

Possible Structures of Chelate Ring in Complexes
Involving 1-Methoxy-2-Propanol

TABLE XI

MOLECULAR WEIGHT OF TRIETHYLAMINE BY FREEZING POINT DEPRESSION OF BENZENE

Concentration TEA in Benzene, g/l	M. W. (Theoretical = 101)
9.1	99
27.3	99
39.4	102
50.5	103
52.5	104

TABLE XII

COMPLEX FORMATION IN MIXTURES OF
1-METHOXY-2-PROPANOL AND TRIETHYLAMINE
BY FREEZING POINT DEPRESSION OF BENZENE

Conc. of 1-Methoxy- 2-Propanol, g/l	Conc. of TEA, g/l	Calculated M. W.		Experimental M.W. (c)	Catalyst in Com- plex, % $\frac{c-a}{b-x} \times 100$
		No Complex (a)	100% Complex (b)		
54.8	0	90	-	124.5	-
54.8	10.5 ¹⁾	120	149	126	21
54.8	29.3 ¹⁾	114	192	127	17
54.8	40.3 ²⁾	114	219	128	13

1) M.W. of TEA = 99

2) M.W. of TEA = 102

complex formation between alcohols (1-methoxy-2-propanol) and catalysts DBTDL and TEA. The results with DBTDL confirm the evidence that was previously (12) obtained by means of NMR data.

Efforts have also been made to find evidence of complex formation between these two catalysts and isocyanates. Using the same technique as described for our alcohol-catalyst work (molecular weights by the freezing point depression of benzene), mixtures of phenyl isocyanate and DBTDL have been studied. It can be seen from Table XIII that no evidence of complex formation between phenyl isocyanate molecules could be obtained. No change in molecular weight was evident with increasing concentrations of phenyl isocyanate in benzene; the theoretical molecular weight of 119 was obtained in each of the three concentrations shown in Table XIII.

In Table XIV measurements on mixtures of phenyl isocyanate and DBTDL are shown resulting in molecular weight values that are indicative of a significant amount of complex formation. The measurements indicate that as much as 40-50% of the DBTDL molecules are tied up in complexes with phenyl isocyanate. Significantly larger concentrations of the catalyst seem to be involved in isocyanate complexes than were previously shown to be the case with the alcohol complexes. It should be noted, however, that in commercially practical urethane reactions, much lower concentrations of catalysts are usually employed. This comparison, of ease or quantity of complex formation, may not be equivalent at these lower catalyst concentrations.

In Table XV are listed measurements indicative of the ability of TEA to form complexes with phenyl isocyanate. The molecular weight values indicate that a significant amount of complex formation has been obtained. It is again of

TABLE XIII

MOLECULAR WEIGHT OF PHENYL ISOCYANATE
BY FREEZING POINT DEPRESSION OF BENZENE

Concentration Phenyl Isocyanate in Benzene, g/l	M. W. (Theoretical = 119)
47.6	118.6
52.4	119.1
63.1	119.0

TABLE XIV

COMPLEX FORMATION IN MIXTURES OF
PHENYL ISOCYANATE AND DIBUTYLIN DILAURATE
BY FREEZING POINT DEPRESSION OF BENZENE

Conc. of Phenyl Isocyanate, g/l	Conc. of DBTDL, g/l	Calculated M.W.		Experimental M.W. (c)	Catalyst in Com- plex, % $\frac{c-a}{b-a} \times 100$
		No Complex (a)	100% Complex (b)		
47.6	0	119	-	119	-
52.4	44.9 ¹⁾	187	222	204	49
70.2	157.1 ²⁾	266	392	322	44
46.4	224.4 ²⁾	350	691	482	39

¹⁾ M.W. of DBTDL = 561

²⁾ M.W. of DBTDL = 575

TABLE XV

COMPLEX FORMATION IN MIXTURES OF
PHENYL ISOCYANATE AND TRIETHYLAMINE
BY FREEZING POINT DEPRESSION OF BENZENE

Conc. of Phenyl Isocyanate, g/l	Conc. of TEA, g/l	Calculated M. W.		Experimental M.W. (c)	Catalyst in Com- plex, % $\frac{c-a}{b-a} \times 100$
		No Complex (a)	100% Complex (b)		
61.9	0	119	-	119	-
61.9	8.9 ¹⁾	116	132	120	25
61.9	18.8 ¹⁾	113	156	122	21
61.9	27.7 ¹⁾	112	172	132	33

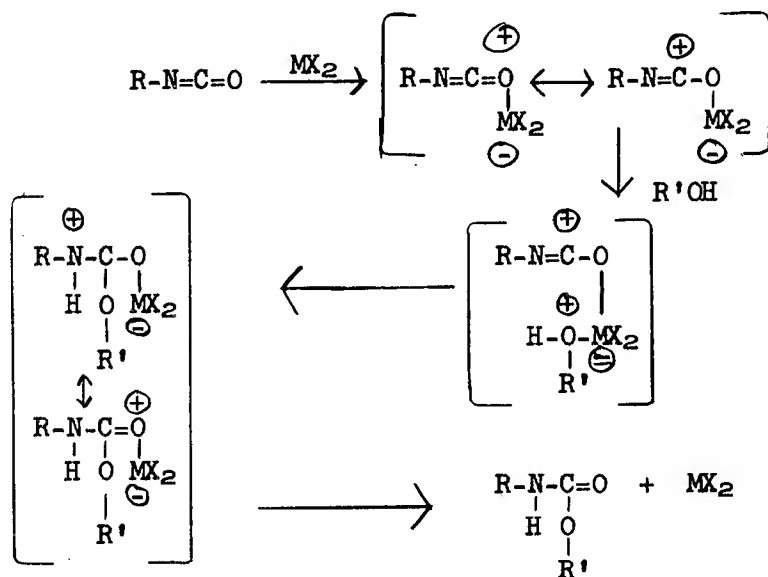
¹⁾ M. W. of TEA = 99

TABLE XVI

COMPLEX FORMATION IN MIXTURES OF n-NONANE
AND DIBUTYLtin DILAURATE BY FREEZING
POINT DEPRESSION OF BENZENE

Conc. of n-Nonane, g/l	Conc. of DBTDL, g/l	Calculated M. W.		Experimental M.W.	Conc. Complex, %
		No Complex	100% Complex		
10.2	0	128	-	127.5	-
10.2	241.5	503	597	502	0
41.0	241.5	381	673	383	0

The results which we obtained for complex formation between metal catalysts such as tin and lead compounds, and 1-methoxy-2-propanol and phenyl isocyanate, respectively, were strong experimental confirmation for ternary complex formation which was first proposed by Britain and Gemeinhardt (24). These investigators postulated complex formation between the metal compound, the isocyanate and the hydroxyl compound. Complex formation could occur in two steps with either the hydroxyl or the isocyanate compound reacting first. The mechanism is shown for the case in which the isocyanate complexes first with the metal compound:



According to this mechanism, both the isocyanate and the hydroxyl compound are brought in close proximity to each other by means of the metal compound. This would also explain the high activation of aliphatic isocyanates by metal catalysts since aliphatic isocyanates are not sterically hindered and, hence, should be able to form more readily these complexes.

Smith (13) has criticized this mechanism because it requires an attack of one electron deficient center on another, and, therefore, would be unlikely to

occur. He proposed an alternate mechanism in which the metal complexes with the alcohol at some site other than the reactive hydroxyl group.

In the case of 1-methoxy-2-propanol we are dealing with what Robins (25) calls an "activated" alcohol; the introduction of a functional methoxy group in a position α - or β - to the carbon atom carrying the reactive hydroxyl group could be expected to have the following influence: it would increase the stability of the alcohol-metal ion complex when either five, six, or seven membered chelate rings can be formed, and it also would allow the hydroxyl group to retain a larger portion of its nucleophilicity, particularly in complexes which contain the more electronegative metal ions, as indicated in Figure 11.

The tin complex with 1-methoxy-2-propanol is shown in Figure 12 and the tin complex with phenyl isocyanate in Figure 13. Reaction between the ligands of these complexes presumably takes place by an exchange of the ether oxygen in the complex shown in Figure 12 by an oxygen atom that is part of an isocyanate group as seen in Figure 13. This should result in formation of a bridge compound having the structure shown in Figure 14. Since it is possible for more than one of the tin-alcohol or tin-isocyanate complexes to interact, this could easily account not only for the presence of bridge compounds of the type AB, but also of the type A_2B , AB_2 , etc. Urethane formation would then take place by rearrangement of the hydroxyl proton to the nitrogen of the isocyanate group as indicated by the arrow.

Likewise the synergistic action between tin and amine catalysts can be accounted for by the structure in Figure 14 since the isocyanate group can complex with the amine in the manner shown previously.

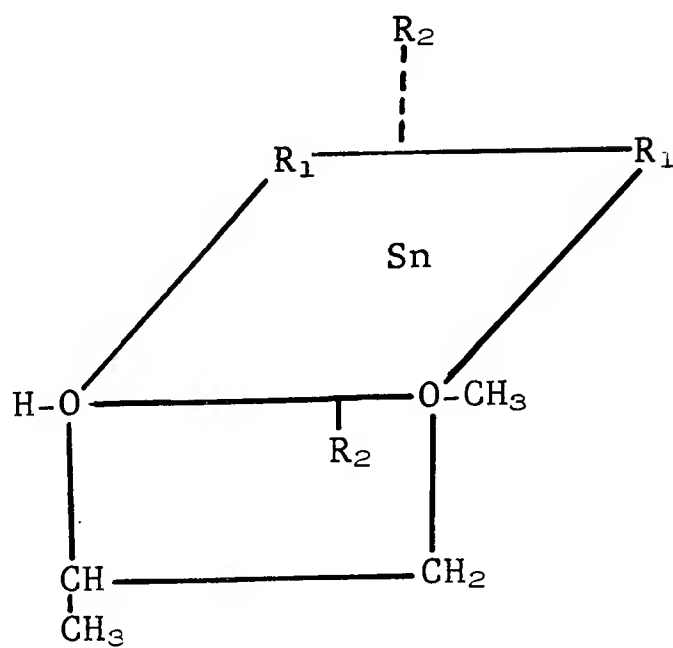


Figure 12

Tin Complex with 1-Methoxy-2-Propano

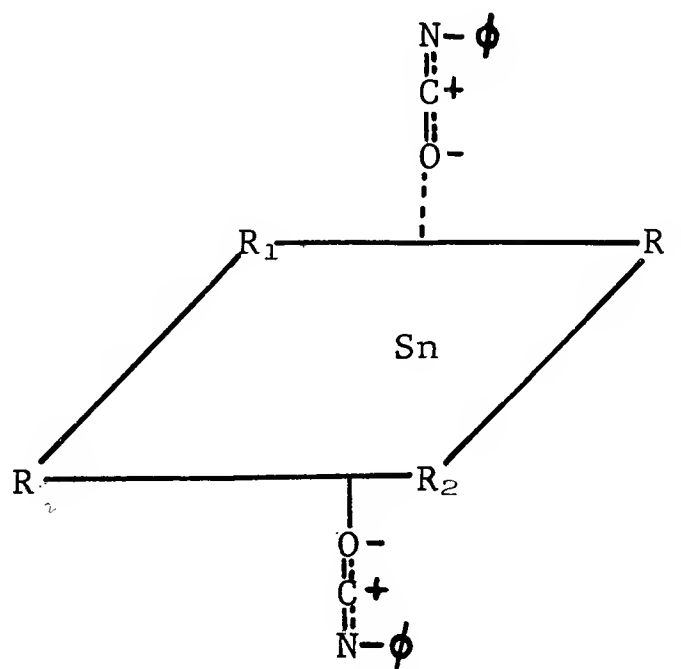


Figure 13

Tin Complex with Phenyl Isocyanate

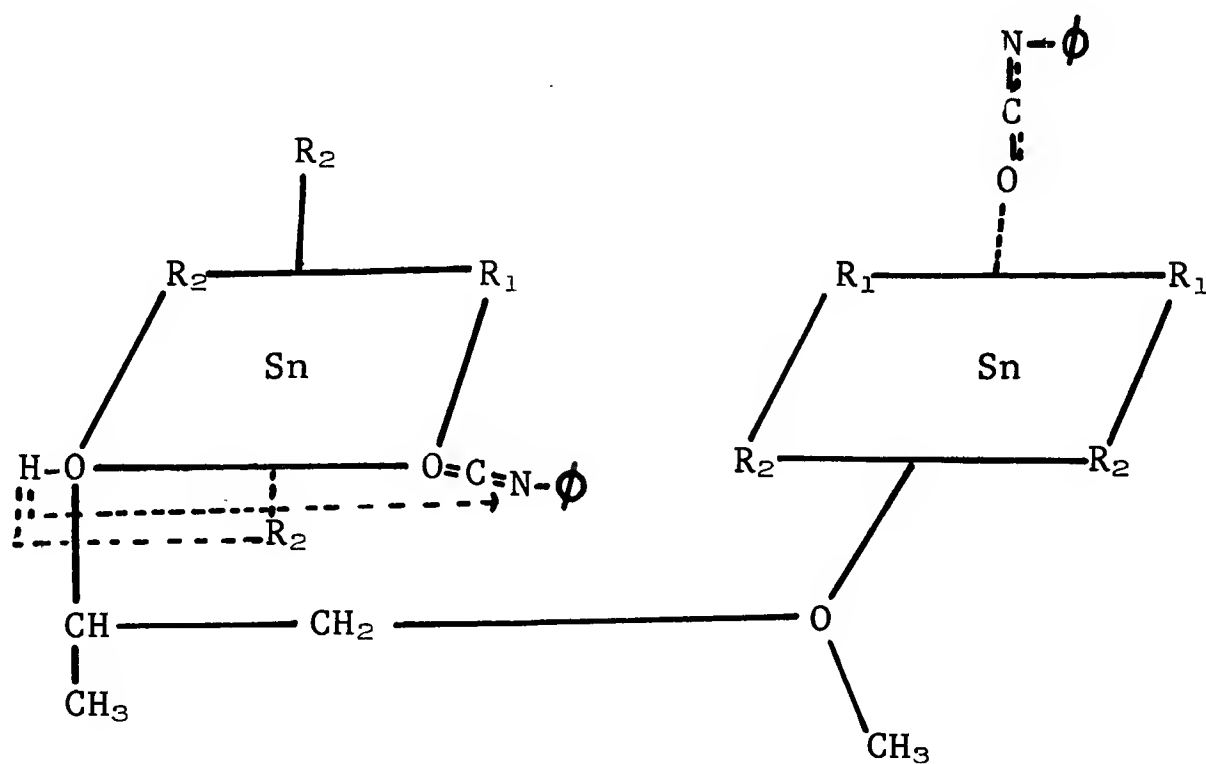


Figure 14

Bridge Complex Between 1-Methoxy-2-Propanol,
Phenyl Isocyanate and Tin

While the relative speed of complex formation is usually very fast, the rate-determining step, the reaction between the ligands after complex formation has taken place, depends upon the coordination number of the metal ion, the configuration of the complex, and the ionic radius of the ion.

References

1. Darr, W. C., P. G. Gemeinhardt and J. H. Saunders, J. Cellular Plastics 2, 266 (1966).
2. Greth, G. G., R. G. Smith and G. O. Rudkin, Jr., J. Cellular Plastics 1, 159 (1965).
3. Baker, J. W. and J. B. Holdsworth, J. Chem. Soc. 713 (1947).
4. Alzner, B. G. and K. C. Frisch, Ind. Eng. Chem. 51, 715 (1959).
5. Mort, F., J. Oil and Colour Chem. Assoc. 45, 95 (1962).
6. Wolfe, H. W., Jr., E. I. duPont de Nemours & Co., Elastomers Foam Bulletin "Tin Catalyst Activity in Urethane Foam," Feb. 24, 1961.
7. Stengard, R. H., Section IX "Rigid Urethane Foams" in "Handbook of Foamed Plastics" by R. J. Bender, Lake Publishing Corp., Libertyville, Ill., 1965, p. 126.
8. Wolfe, H. W., Jr., E. I. duPont de Nemours & Co., Elastomers Foam Bulletin "Catalyst Activity in One-Shot Urethane Foam," Mar. 16, 1960.
9. Rogers, A. F., Union Carbide Corp., "Catalysis of the Reactions Involved in Making Flexible Urethane Foams," Polymer Conference on Cellular Plastics, Wayne State Univ., May 1966.
10. Rand, L., B. Thir, S. L. Reegen and K. C. Frisch, J. Appl. Polymer Sci. 9, 1787 (1965).
11. Frisch, K. C., S. L. Reegen and B. Thir, J. Polymer Sci., in press.
12. Frisch, K. C., S. L. Reegen, W. V. Floutz and J. P. Oliver, J. Polymer Sci., in press.
13. Smith, H. A., J. Appl. Polymer Sci. 7, 85 (1963).
14. Pestemer, M. and D. Lauerer, Angew. Chem. 72, 612 (1960).
15. Farkas, A. and P. F. Strohm, I.&E.C. Fundamentals 4, No. 1, 32 (1965).

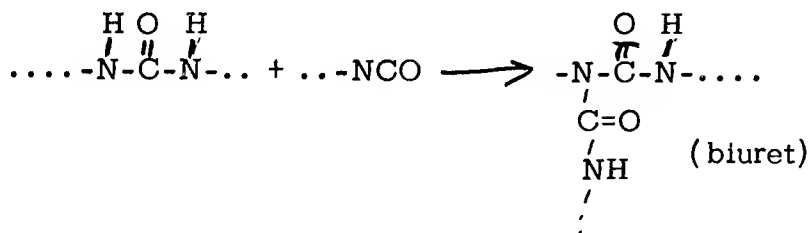
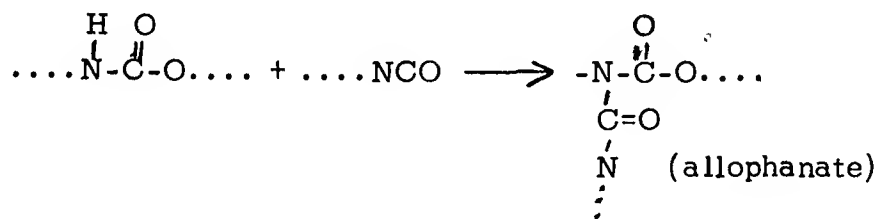
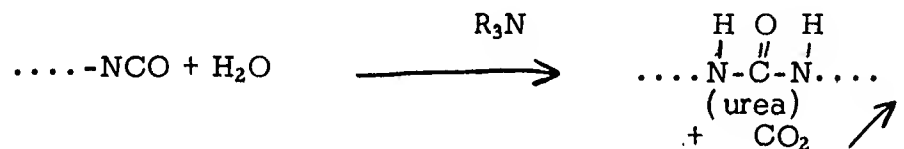
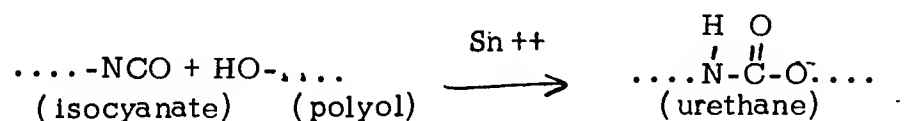
16. Sumi, M., Y. Chokki, Y. Nakani, M. Nakabayashi and T. Kanzawa, *Makramol. Chem.* 78, 146 (1964).
17. Baker, J. W. and J. Gaunt, *J. Chem. Soc.* 9 (1949).
18. Baker, J. W. and J. Gaunt, *ibid.*, 19 (1949).
19. Baker, J. W., M. M. Davies and J. Gaunt, *ibid.*, 24 (1949).
20. Baker, J. W. and J. Gaunt, *ibid.*, 27 (1949).
21. Baker, J. W. and D. N. Bailey, *ibid.*, 4649 (1957).
22. Baker, J. W. and D. N. Bailey, *ibid.*, 4652 (1957).
23. Baker, J. W. and D. N. Bailey, *ibid.*, 4663 (1957).
24. Britain, J. W. and P. G. Gemeinhardt, *J. Appl. Polymer Sci.* 4, 207 (1960).
25. Robins, J., *J. Appl. Polymer Sci.* 9, 821 (1965).

STABILIZATION OF POLYURETHANE FOAM ROLE OF THE SILICONE SURFACTANT

Bernard Kanner

Union Carbide Corporation
 Sterling Forest Research Center
 Tuxedo, New York

The process of forming a polyurethane foam can be described chemically by the following equations¹:



The completion of these reactions results in polymer chain extension, crosslinking, gas generation and in the presence of a silicone surfactant, foam formation. The physical phenomena which accompany these reactions are even more complex and less well understood. The many developments within polyurethane foam technology and the widespread application of its products have led to numerous product and process variants. Each of these has necessitated appropriate adjustments in the many parameters which make up a polyurethane foam system. Perhaps the most striking change was the transition during 1956 to 1958 from a prepolymer system based on polyesters

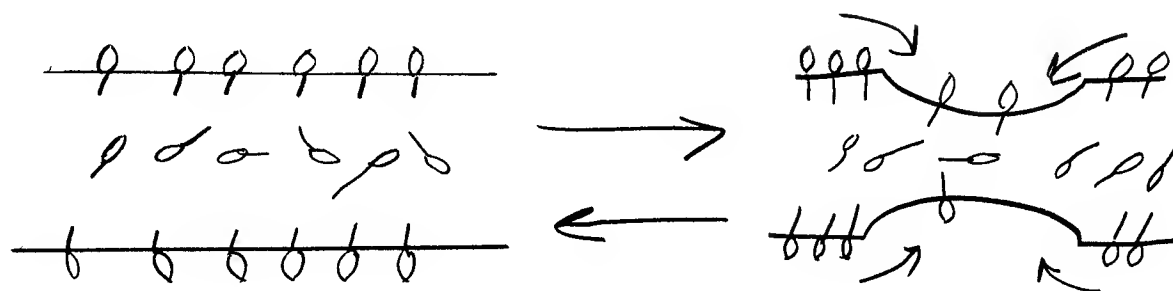
or polyethers to a "one-shot" system based on polyether triols. The prepolymer process required two steps. In the first, the isocyanate is reacted with the polyol resin to form an isocyanate-terminated polymer. This polymer is then foamed in the presence of a silicone oil by subsequent reaction with water. For this highly viscous system, the surfactant requirements are relatively modest. The rate of liquid film drainage and bubble collapse is inherently much slower in a high viscosity (10,000 to 30,000 cp.) system. In the one-shot system all of the components are mixed together and allowed to react simultaneously. A substantially increased stabilizing ability is demanded of the surfactant, a dimethylsilicone-polyether copolymer, for this very low viscosity system (120 cp.). Without the availability of silicone-polyether surfactants the commercial development and rapid growth of one-shot flexible foam would not have been possible.^{2,3} This is the dominant foam system today and an understanding of the role of silicone surfactants in flexible polyether foam can be used to rationalize many similar phenomena noted in other systems.

Throughout the process of preparing a flexible one-shot foam, the silicone surfactant is responsible for several critical and related functions. These are best understood if we consider the basic forces believed to be operative in the stabilization of a foam bubble. Four mechanisms or explanations have been advanced to account for the stability of aqueous foams.^{4,5} They are:

- (1) Gibb's Surface Elasticity Theory
- (2) Marangoni's Surface Elasticity Theory
- (3) Surface Transport Theory
- (4) Surface Viscosity and Bulk Viscosity

Although there is supporting evidence for these theories in aqueous foam systems, there is essentially no published data to support any of these rationals for polyurethane foam. Nevertheless, a reasonable working hypothesis is provided by a combination of the second and third theories.

As the thickness of a bubble wall progressively thins due to liquid drainage, it becomes more susceptible to film rupture. In the presence of a surfactant which can lower the surface tension of the system, an important stabilizing mechanism serves to prevent or delay rupture of the wall and bubble collapse. As thermal shock or other transient forces induce a momentary thinning of a bubble wall, there is a temporary depletion or



○ Surfactant molecule

lowering of the surface concentration of the surfactant. This results in a temporary increase in surface tension in the region of the thinned area. This is rapidly offset by the migration of surfactant molecules from the adjacent surface layers to restore the original equilibrium surface tension. As the surfactant molecules migrate to the thinned area, liquid medium molecules attracted to the surfactant by van der Waal forces accompany the surfactant tending to restore the original thickness of the bubble wall.

In order for this mechanism to be operative, a surfactant must be used which meets several critical criteria. They are:

- (1) Ability to lower the surface tension of the medium
- (2) Appropriate dynamic surface tension lowering ability
- (3) van der Waal attractive forces of the surfactant for the medium molecules

The first requirement is sufficient to rule out essentially all but silicone surfactants as suitable for polyurethane foam stabilization. The major component of urethane foam, a polyoxypropylene triol (LG-56), has a quite low surface tension (32 dynes/cm. at 25°C.). Although a number of organic surfactants can lower the surface tension of water below this level they lose their surfactant characteristics in LG-56. Surfactants based on hydrocarbons as hydrophilic groups are not amphipathic (having a dual nature) in many organic liquids. For although hydrocarbons are insoluble in water, they are soluble in a wide variety of organic liquids. This is illustrated by a comparison of the surface tension lowering ability of a number of surfactants in the polyether triol summarized in Table I.^b Although dimethylsilicone polymers, dimethylsilicones-polyether and fluoro-carbon-polyether surfactants lower the surface tension of LG-56, the

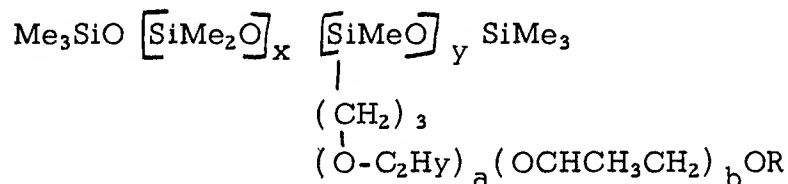
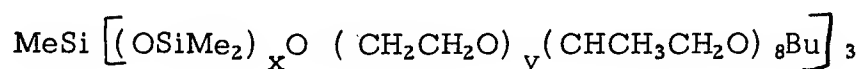
TABLE I
SURFACE TENSION LOWERING OF POLYPROPYLENE GLYCOL
LG-56 BY SURFACTANTS

<u>Surfactant</u>	<u>Surface Tension (dynes/cm.)</u> <u>1 Wt-% Solution (25°C)</u>
none	32.0
MD ₃ M' (EO) _{8.2} ^a Me	30.2
MD ₆ M' (EO) _{12.8} ^a Me	27.2
MD ₉ M' (EO) _{17.3} ^a Me	23.4
MM' (EO) ₃ Me	31.5
-520 ^b	25.6
Tergitol TMN	32.0
Brij 72	31.8
Aerosol OT	31.2
Tergitol 12P6	31.9
HCF ₂ (CF ₂) ₆ CH ₂ OH	32.0
Sodium Lauryl Sulfate	insoluble
L-1006 ^c	24.0

- a Copolymers prepared from undistilled methoxypolyethylene glycol 350, 550 or 750.
- b U. C. C. Silicones Division copolymer of methylsiloxane with ethylene oxide-propylene oxide polyether.
- c 3M Fluorocarbon nonionic surfactant.

hydrocarbon surfactants are essentially without effect. A number of hydrocarbon surfactants have the potential of lowering the surface tension of LG-56; however, solubility of the hydrocarbon portion of the surfactant eliminates the driving force usually present.

Silicone surfactants are based on high molecular weight silicone polymers which are not only insoluble in water but also have unusually low surface tensions (20 dynes/cm.) The behavior of typical silicone and hydrocarbon nonionic surfactants is compared in Figure 1⁶.



Fluorocarbon surfactants and dimethylsilicone oils can also lower the surface tension of polyethers but do not stabilize polyurethane foam. They do not meet the second and third requirements of a suitable foam surfactant.

In aqueous systems it has been demonstrated experimentally that dynamic surface tension - the rate at which a newly formed surface approaches its equilibrium - is a key factor in foam stabilization. To produce a stable foam a newly formed surface should not reach its equilibrium value too rapidly. In Figure 2 the dynamic surface tension of two silicone surfactants are compared.⁷ Curve A represents a copolymer rich in silicone and a marginal foam stabilizer. Curve B is a normal surfactant which is an effective foam stabilizer. The slope of Curve A is greater, indicating a more rapid dynamic response, probably too rapid for the Marangoni and surface transport effects to come into play.

In addition to the critical role of bubble stabilizer, the silicone surfactant significantly influences other stages in the formation of a polyurethane foam.⁸ Tables II and III summarize the components and process of preparing a flexible one-shot polyether foam.

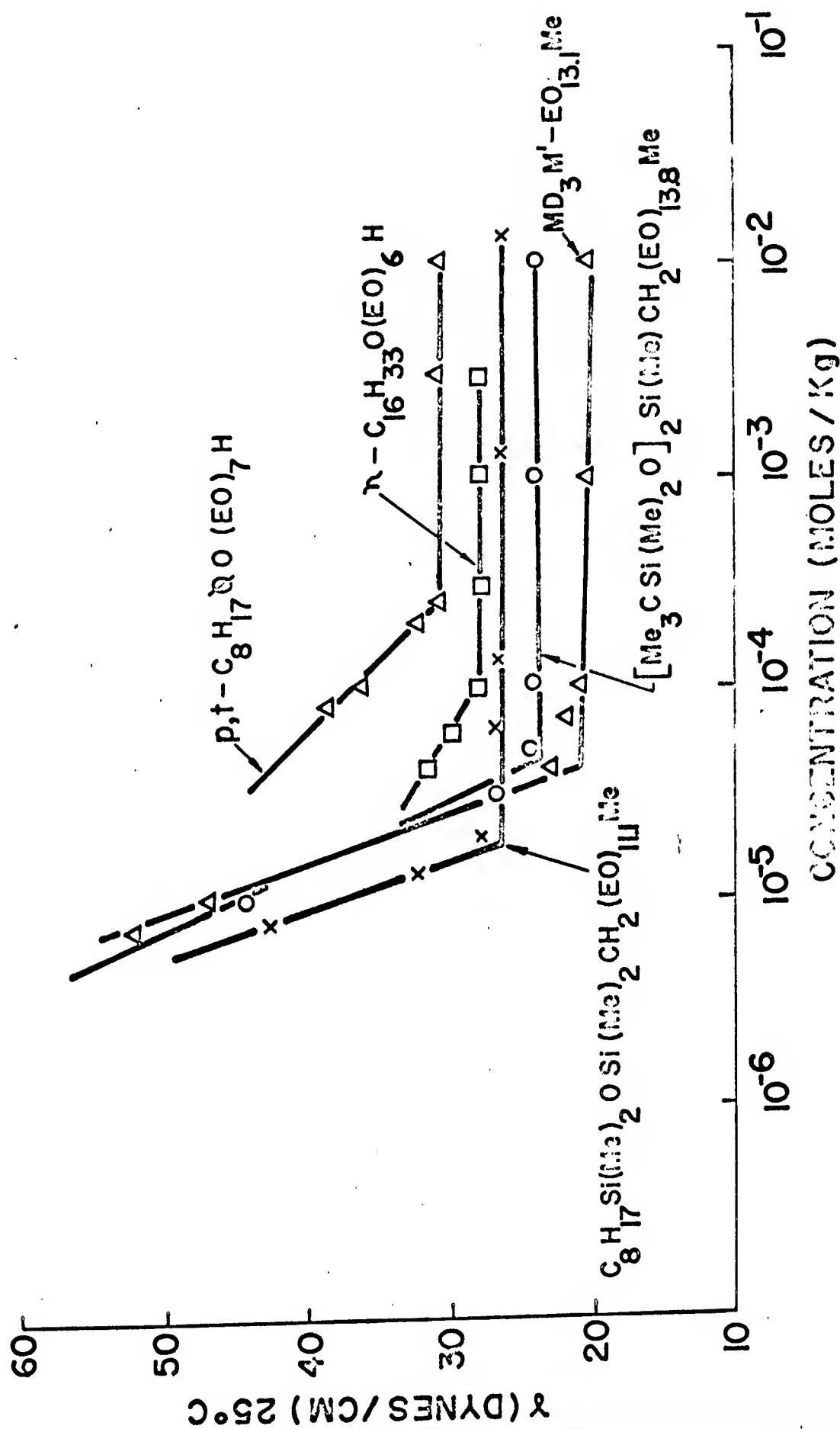


FIGURE 1 Surface tension vs. concentration for hydrocarbon and polyether copolymers

FIGURE 2

The dynamic surface tension of silicone-oxyalkylene copolymers in 1% aqueous solution.

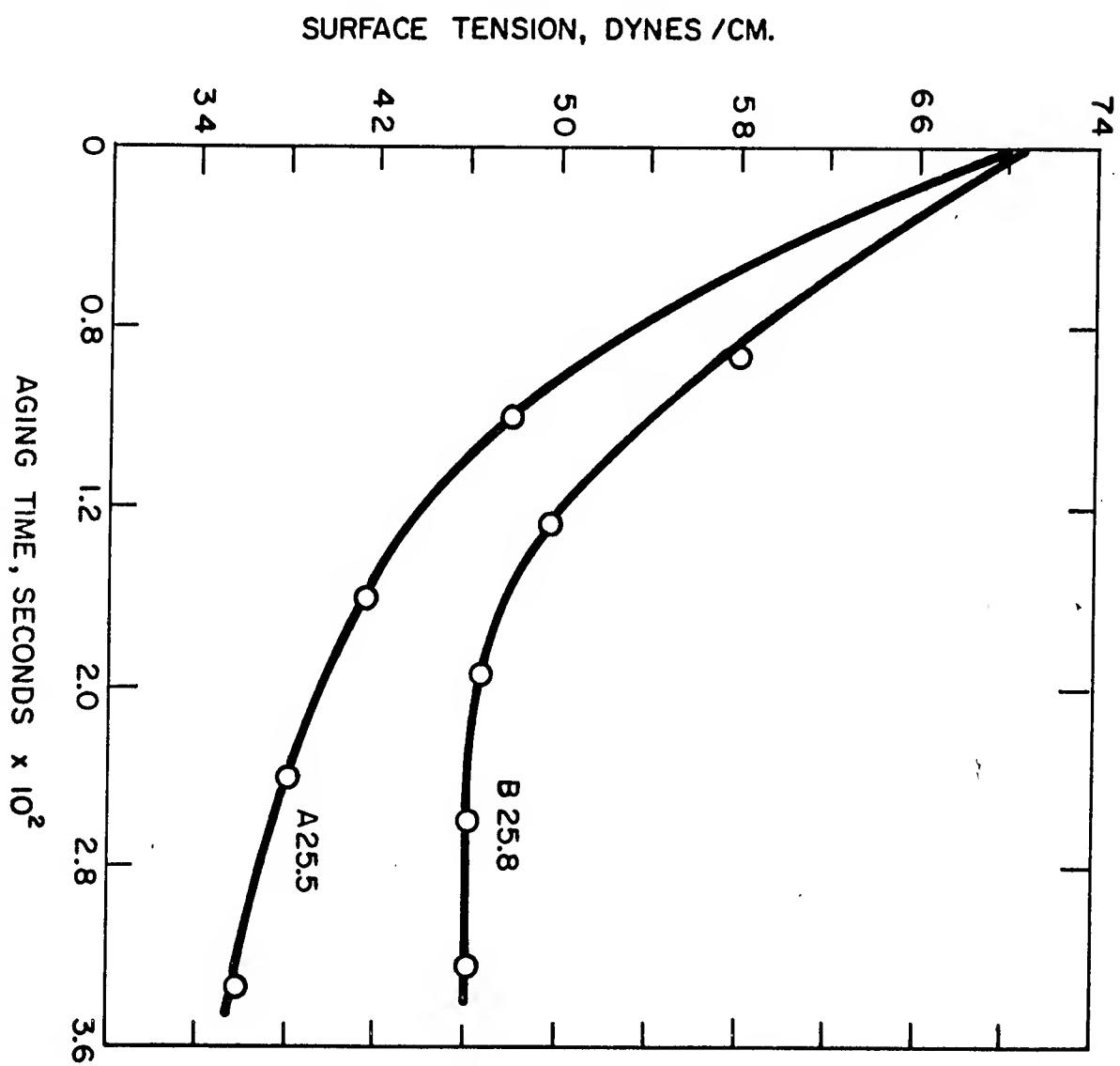


TABLE II

COMPONENTS USED IN A TYPICAL FLEXIBLE
ONE-SHOT URETHANE FOAM

<u>Ingredient</u>	<u>Concentration</u>
LG-56 (A polypropylene triol)	100
Toluene diisocyanate	50
Tertiary amines	0.3
Stannous octoate	0.3
H ₂ O	4.0
L-520 (A silicone- polyether copolymer)	1.2

TABLE III

STEPS IN THE PREPARATION OF A FLEXIBLE URETHANE FOAM

<u>Step</u>	<u>Time (sec.)</u>	<u>Remarks</u>
Pre-mix of all ingredients except toluene diisocyanate		
Agitation of pre-mix	0	Air is mixed in.
Addition of toluene diisocyanate. Continue stirring.	7	Reaction begins. Temperature and viscosity of system increase.
Stop stirring - pour	15	
	20	Cream time. Foam Rise begins.
	100	Rise is complete Cells open
Foam is cured at 100°C. for 15 minutes		

During steps II, III and IV the key processes of bubble introduction, bubble growth, bubble stabilization and cell opening take place. Mixing of the foam components with a silicone surfactant (Steps II and III) results in an appreciable incorporation of air in the form of tiny air bubbles. In the absence of a silicone surfactant far fewer bubbles and a much smaller volume of air are incorporated into the reaction mixture. The bubbles that are incorporated by the mixing action serve as sites for carbon dioxide evolution, and in the presence of a surfactant are sufficient in number to account for all of the cells in the final foam. Thus nucleation of new bubbles is not essential to this process.⁸ Without a surfactant, carbon dioxide boils out of the reaction mixture (bubble collapse predominates due to lack of stabilization) but gas evolution is slowed. Although the carbon dioxide gas is being generated in solution, in the absence of an adequate number of bubble sites for gas evolution, the solution becomes supersaturated. During foam rise (Step IV) the silicone polyether surfactant stabilizes the bubbles by the mechanism previously discussed. Essentially all of the carbon dioxide gas generated evolves into the existing bubbles but is retained by the foam matrix. Air samples taken above the rising foam show no surge in carbon dioxide content until rise is completed and the cells open. As the foam rises, the cell walls between bubbles progressively thin, and as foam rise is completed, the cell walls rupture to give an open celled foam. The delicate balance between completion of foam rise and cell opening is controlled by the selection and concentration of the amine and tin catalysts. Thus, the principal functions of the silicone surfactant are (1) the introduction of many small bubbles which serve as the sites of carbon dioxide evolution; (2) stabilization of the foam bubbles during expansion of the foam; and (3) control of bubble wall drainage so that opening of the foam will not precede completion of foam rise.

MEMORANDUM

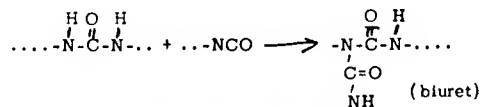
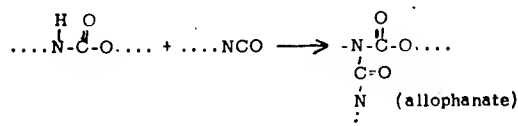
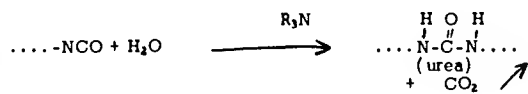
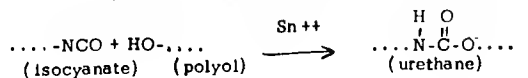
TO: Attendees, Polymer Conference Course Number One
Cellular Plastics Technology

FROM: Professor Irving N. Einhorn

SUBJECT: Addition to Conference Preprint

DATE: August 1, 1967

Enclosed please find copies of the slides shown by
Dr. Bernard Kanner of the Union Carbide Corporation.



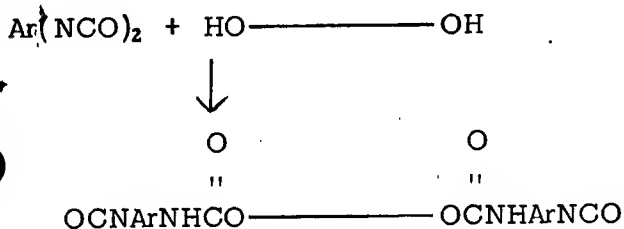
Slide 1

Prepolymer Process
High Viscosity
Methylsilicone Oil
Stabilizer

1956-8

One Shot Process
Very Low Viscosity
Silicone-Polyoxyalkylene
Copolymer Stabilizer

Slide 2



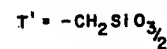
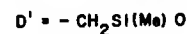
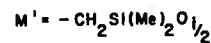
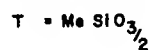
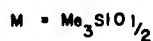
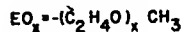
Prepolymer

- I
 - a. Flexible
 - b. Rigid
- II
 - a. Prepolymer
 - b. Quasi-Prepolymer
 - c. One-Shot
- III
 - a. Polyether
 - b. Polyester
 - c. Others

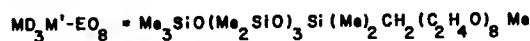
Slide 3

Slide 4

NOMENCLATURE PRACTICES



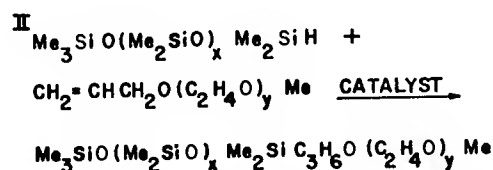
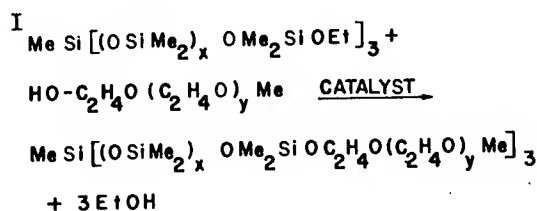
THUS:



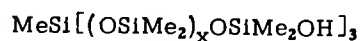
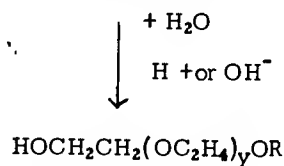
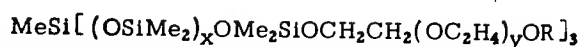
Slide 5

Slide 6

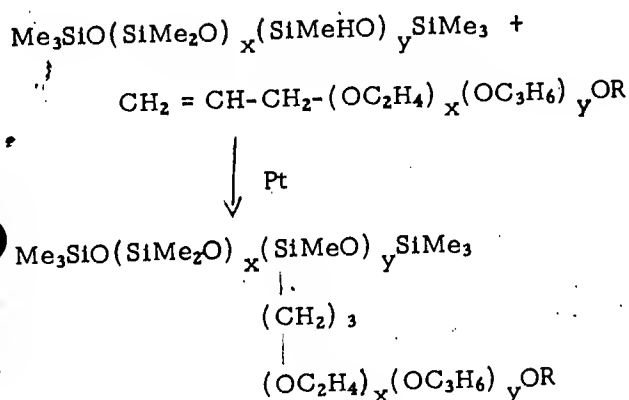
METHODS OF PREPARATION



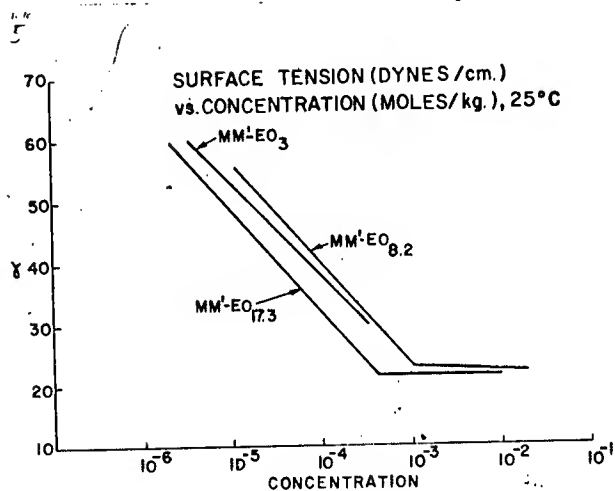
Slide 7



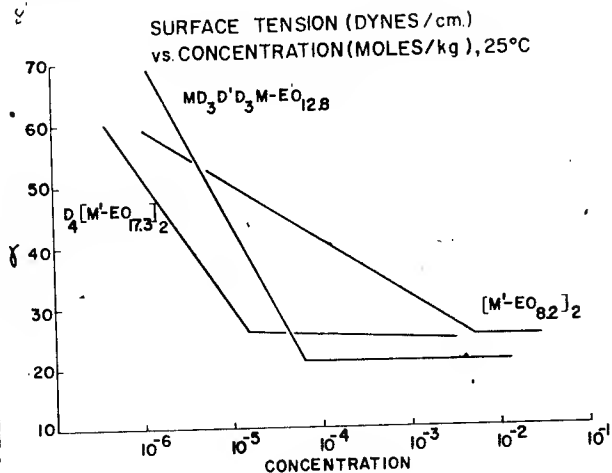
Slide 8



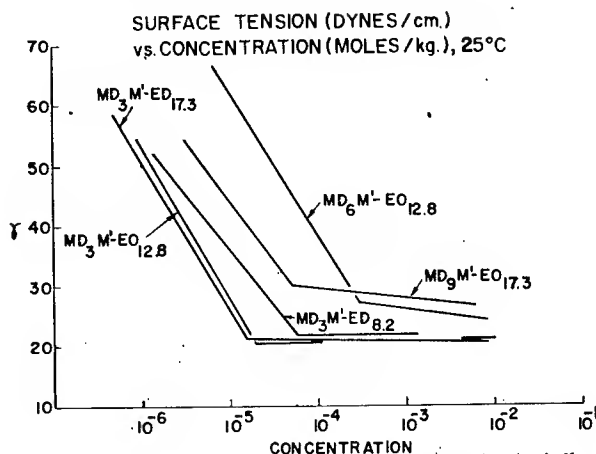
Slide 9



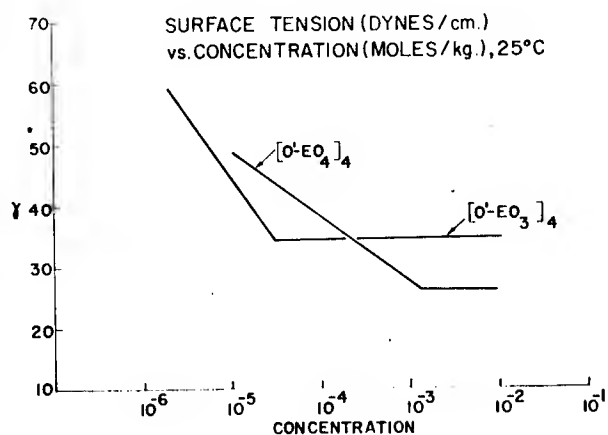
Slide 10



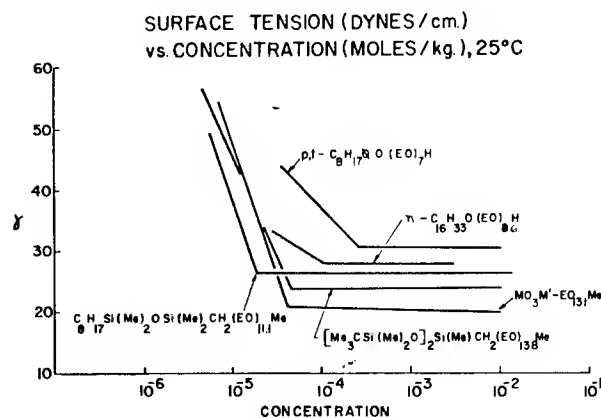
Slide 11



Slide 12



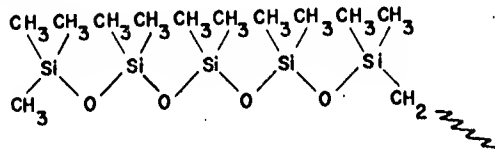
Slide 13



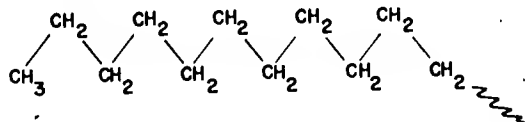
slide 14

SURFACTANT HYDROPHOBES

SILICONE



HYDROCARBON



Slide 15

HYDROCARBON, HYDROCARBON-SILOXANE AND SILOXANE SURFACTANTS

SURFACTANT HYDROPHOBE	γ , IOWT. % aq. SOL'N. DYNES/cm.
$(Me)_3CCH_2C(Me)_2O-$	30.5
$CH_3(CH_2)_{15}O-$	26.4
$CH_3(CH_2)_7Si(Me)_2O_2Si(Me)_2CH_2-$	26.3
$(Me)_3C-Si(Me)_2O-Si(Me)_2C(Me)_3$	23.3
$Me_3SiO(Me_2SiO)_3Si(Me)_2CH_2-$	20.4

Slide 16

COHESIVE FORCES OF HYDROCARBONS, SILOXANES AND FLUOROCARBONS

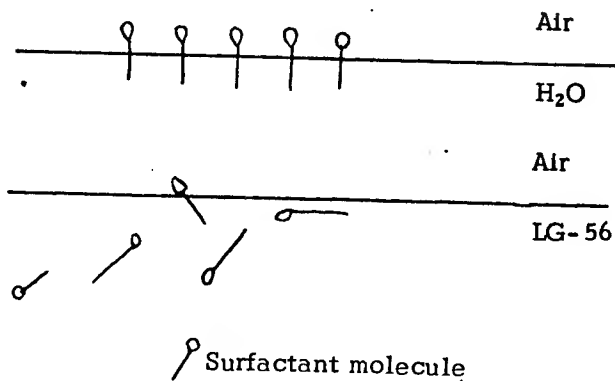
HYDROPHOBE	No. OF ATOMS	SURFACE TENSION	SOLUBILITY PARAMETER
$CH_3(CH_2)_{26}CH_3$	26	21.8	7.6
$(CH_3)_3CCH_2CH(CH_3)_2$	26	18.3	6.9
$(CH_3)_3SiOSi(CH_3)_3$	27	15.7	6.0
$CF_3(CF_2)_6CF_3$	26	13.6	5.7
$CH_3(CH_2)_{10}CH_3$	38	25.0	7.8
$(CH_3)_3SiOSi(CH_3)_2OSi(CH_3)_3$	37	16.9	5.5
$CF_3(CF_2)_{10}CF_3$	38	M.P. 74°C	ΔH_v NOT AVAILABLE

Slide 17

SURFACE TENSION LOWERING OF POLYPROPYLENE GLYCOL LG-56 BY SURFACTANT

SURFACTANT	SURFACE TENSION DYNES/cm, 25°C
NONE	32.0
$MO_3M'-EO_{12}$	30.2
$MO_3M'-EO_{12.8}$	27.2
$MO_3M'-EO_{17.3}$	23.4
$MM'-EO_3$	31.5
L-530	25.6
L-520	25.0
TERGITOL TMN	32.0
BRIJ-72	31.8
AEROSOL OT	31.2
TERGITOL 12-P-6	31.9
HICF ₂ 16 CH ₂ OH	32.0
L-1006 FLUOROCARBON NONIONIC	24.6
SODIUM LAURYL SULFATE	INSOLUBLE

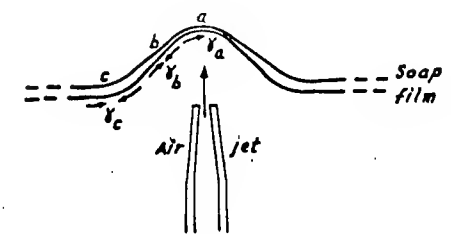
Slide 18



slide 19

- (a) What is the physical factor which distinguishes foaming from non-foaming solutions?
- (b) What mechanism or mechanisms can account for the stability of foams.

slide 21



Local thinning of a soap film under the impact of a gas jet

slide 23

Pure Liquids
or
Solutions of
Similar
Liquids

No Foam.

Liquids and Solutes
Some lowering of
Surface Tension

Short lived foam.

Liquids and Solutes
Substantial lowering
of Surface Tension

Meta Stable Foam.

slide 20



Stages in the bursting of a single bubble on the surface of water. (Drawings by Arthur Smith from the high-speed photographs of Newitt, Dombrowski and Knelman.)

slide 22

Gibbs Surface Elasticity (1878)

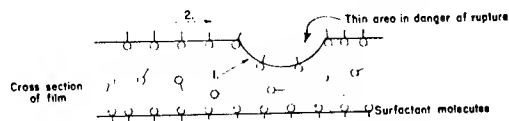
Marangoni Surface Elasticity (1865)

Plateau Surface Viscosity and
Bulk Viscosity (1873)

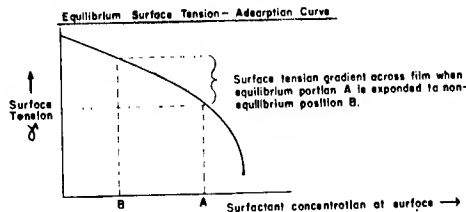
Derjaguin Electrical Double
Layer Repulsion (1953)

slide 24

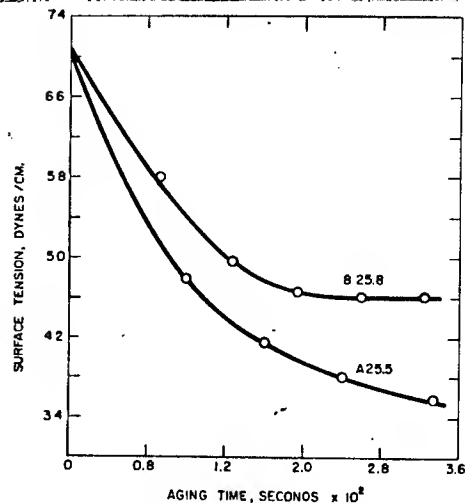
Foam Stabilization - The Marangoni Effect



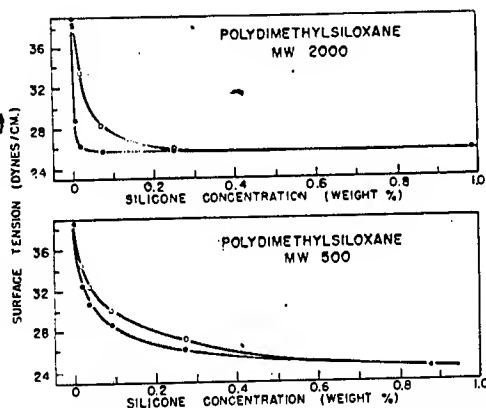
1. Movement of surfactant from solution to area of low adsorption density.
2. Surface migration of molecules of surfactant to thin area to repair film.



Slide 25

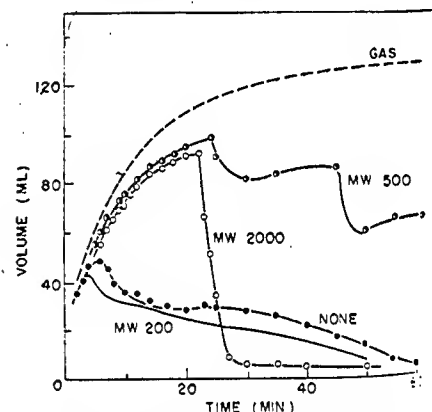


Slide 26



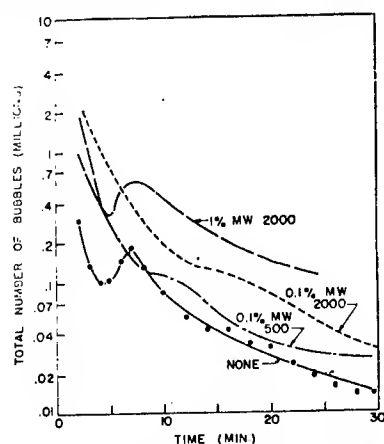
—Effect of polydimethylsiloxane on the surface tension of PTMEG-3000 (circle = fresh surface, dot = surface aged 24 hours).

Slide 27



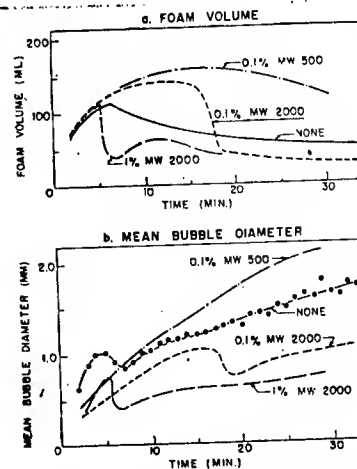
—Effect of polydimethylsiloxane on foaming. Silicone concentration 0.1 weight %, molecular weight as indicated (solid line = foam volume, dotted line = total gas volume).

Slide 28



—Time dependence of total bubble number (silicone concentration and molecular weight as indicated).

Slide 29



—Time dependence of foam volume and bubble size (silicone concentration and molecular weight as indicated).

Slide 30

- (a) Introduction of Bubbles.
- (b) Importance of Nucleation.
- (c) Bubble Coalescence.
- (d) Rate of Gas Evolution.

Slide 31

COMPONENTS USED IN A TYPICAL FLEXIBLE
ONE-SHOT URETHANE FOAM

Ingredient	Concentration
LG-56 (A polypropylene triol)	100
Toluene diisocyanate	50
Tertiary amines	0.3
Stannous octoate	0.3
H ₂ O	4.0
L-520 (A silicone- polyether copolymer)	1.2

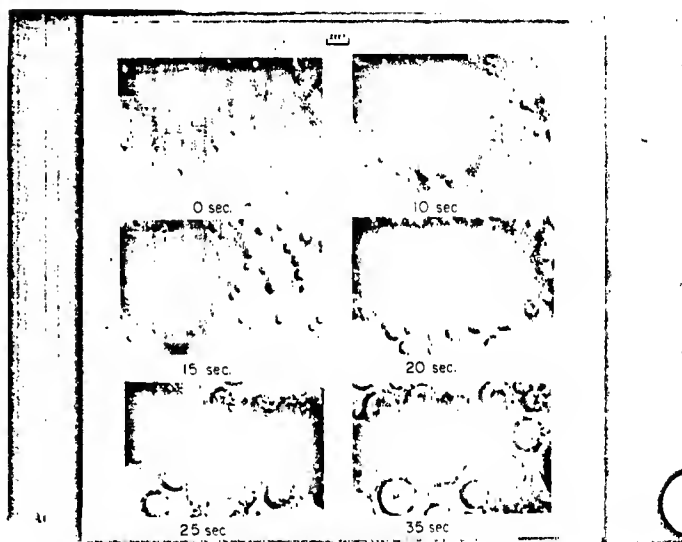
slide 32

STEPS IN THE PREPARATION OF A FLEXIBLE URETHANE FOAM

Step	Time (sec.)	Remarks
Pre-mix of all ingredients except toluene diisocyanate		
Agitation of pre-mix	0	Air is mixed in.
Addition of toluene diisocyanate. Continue stirring.	7	Reaction begins. Temperature and viscosity of system increase.
Stop stirring - pour	15	
	20	Cream time. Foam Rise begins.
	100	Rise is complete. Cells open.

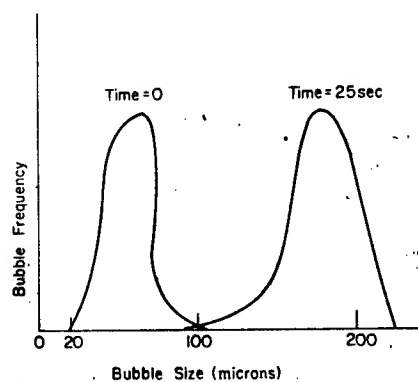
Foam is cured at 100°C.
for 15 minutes

Slide 33

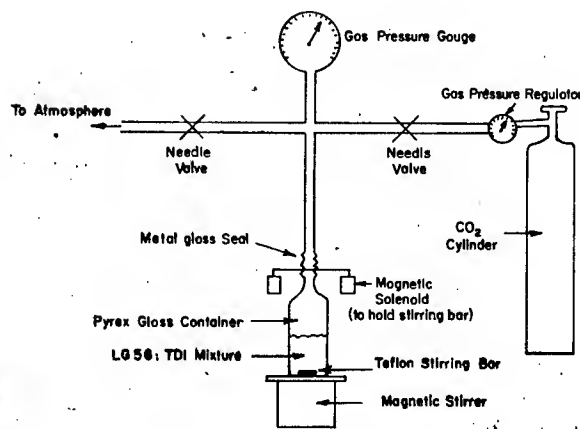


Slide 34

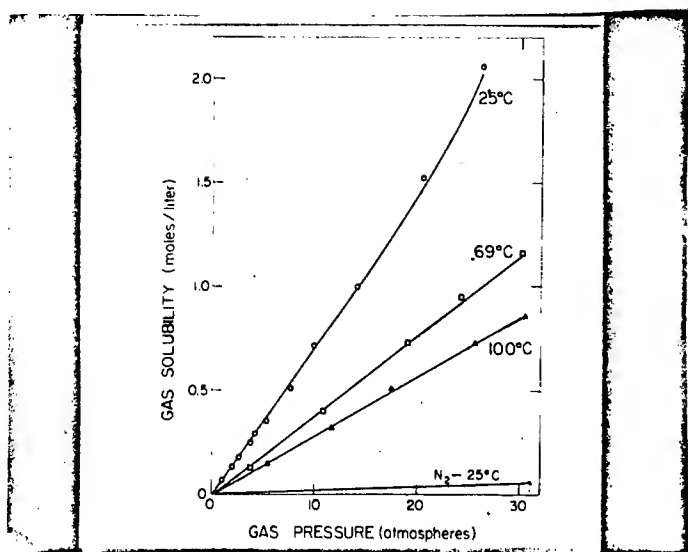
Bubble Size Distribution in
Urethane Foam



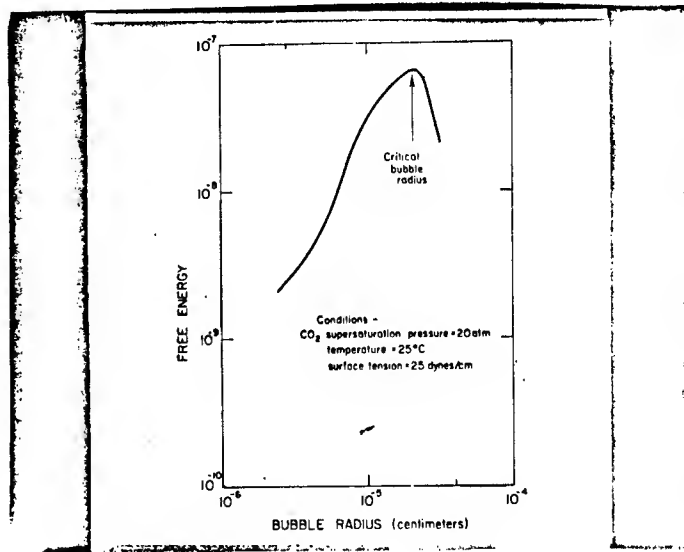
Slide 35



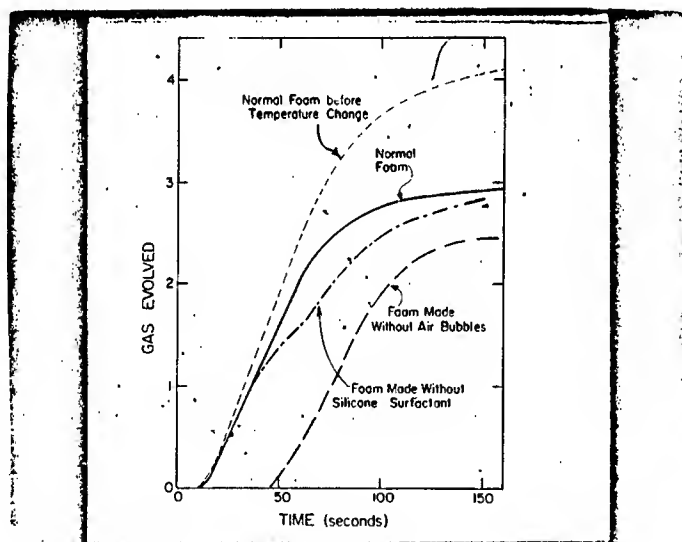
Slide 36



slide 37



slide 38



slide 39

Bibliography

- (1) High Polymer 16, Polyurethanes: Chemistry and Technology I, Chemistry, Chap. III and IV, Saunders, J.H., French, K.C., Interscience Pub., New York.
- (2) Saunders, J.H., Rubber Chem. and Tech., 33(5), 1313, (1960) .
- (3) Buist, J.M., Hurd, R., Lowe, A., Chem. and Ind. 1555 (1960) .
- (4) Kitchner, J.A., Cooper, C.F., Quart. Rev. 71-96 (19) .
- (5) Ewers, W.E., Sutherland, K.L., Austral. J. Sci. Res. A-5, 697-710 (1952) .
- (6) Kanner, B., Reid, W.R., Peterson, I.H., Ind. and Eng. Chem., in press.
- (7) Schwarz, E., Reid, W.G., Ind. and Eng. Chem., 56(9) 28 (1964) .
- (8) Kanner, B., Decker, T.G., Unpublished data (1966) .

10214-03

SPRAY-APPLIED RIGID POLYURETHANE FOAM FOR INDUSTRIAL INSULATION

Carlos J. Hilado
Research and Development Department
Chemicals and Plastics
Union Carbide Corporation
South Charleston, West Virginia

ABSTRACT

In the increasingly competitive climate of the chemical process industries, savings in construction and operating costs are a major factor in financial success. Spray-applied rigid polyurethane foam provides the basis for low-cost thermal insulation systems which reduce both insulation costs in new construction, and reinsulation costs in existing plants.

Experience with the spray foam insulation of over fifty process vessels, storage tanks, and buildings has shown that spray-applied rigid polyurethane foam can cut total insulation job costs to substantially less than half that of conventional insulation. New concepts and techniques may expand the range of applications to cover a temperature span from $-180^{\circ}\text{C}.$ to $+250^{\circ}\text{C}.$

SPRAY-APPLIED RIGID POLYURETHANE FOAM FOR INDUSTRIAL INSULATION

Carlos J. Hilado
Research and Development Department
Chemicals and Plastics
Union Carbide Corporation
South Charleston, West Virginia

INTRODUCTION

In the increasingly competitive climate of the chemical process industries, savings in construction and operating costs are a major factor in financial success. Thermal insulation systems which can be applied at an overall lower cost, can not only lower the construction costs of new plants and the maintenance costs of existing plants, but also reduce the operating costs of both new and existing plants by making it economically feasible to insulate equipment operating at moderate temperatures which were previously not economical to insulate.

To lower-cost thermal insulation materials and systems, the field of industrial insulation therefore offers opportunities not only for market penetration through displacement, but also for new market development through expansion. Spray-applied rigid polyurethane foam is proving to be a material which presents these opportunities.

THE MATERIAL

Rigid polyurethane foam is produced by reacting a polyether or polyester polyol with a diisocyanate or polyisocyanate, under the impetus of an appropriate catalyst. The heat of reaction volatilizes the blowing agent, usually trichlorofluoromethane, producing gas bubbles whose formation is influenced by an appropriate surfactant. For spray application, all of the necessary ingredients are supplied in a two-package system: the resin contains the polyol, catalyst, surfactant, and usually the blowing agent, while the activator contains the isocyanate. When these two streams are mixed either internally or externally by a properly designed spray gun, the resulting mixture can be distributed in the form of a liquid spray on the surface to be insulated. With the rate of reaction determined by proper formulation, the chemical reaction generates a solid polymer while the physical process of foaming is in progress, and the resulting cellular material is an excellent, light weight thermal insulation.

A typical spray-applied rigid polyurethane foam has a density of 2 pounds per cubic foot and a thermal conductivity of less than 0.15 Btu per hour per square foot per degree Fahrenheit per inch of thickness, at 25°C. At this temperature level, a one-inch thickness of rigid polyurethane foam is

equivalent in insulation value to 1-1/2 inches of cellular polystyrene, 2 inches of cork, glass fiber, or mineral fiber, and 3 inches of cellular glass or calcium silicate. Thermal conductivity varies with temperature, as illustrated in Figure 1. As temperature drops progressively below 25°C., condensation of the trichlorofluoromethane blowing agent results in a higher fraction of air in the gas phase until the thermal conductivity approaches that of essentially air-filled material. Further decreases in temperature then reduce thermal conductivity, until, with the condensation of air, the thermal conductivity approaches that of a vacuum-filled material.

As temperature rises progressively above 25°C., the strength of the material begins to decrease, as shown in Figure 2. Increased internal pressure in the gas phase and reduced strength in the solid polymer tend to result eventually in cell-wall rupture and fluorocarbon loss, and the thermal conductivity of the foam then approaches that of an air-filled cellular material. The softening temperature varies with chemical composition (8). Further increases in temperature eventually produce thermal degradation. The extent and manner of degradation are functions of the chemical and physical structure of the foam (2,15,16). With

the better foam materials, the deterioration extends into the foam only a limited distance from the hot surface, and the degraded polymer can have substantial mechanical strength.

Because of its outstanding thermal insulation characteristics, rigid polyurethane foam may be used in applications with temperature differentials as great as 250°C. For example, it might be used to insulate a still column at 230°C. from winter air at -10°C., or a liquid air line at -220°C. from summer air at 30°C. Different portions of the foam would therefore be at substantially different temperatures, and the effective thermal conductivity would have to be a properly weighted average across the entire cross section of foam.

Spray-applied rigid polyurethane foam is usually employed at densities near 2 pounds per cubic foot. In this density range, thermal conductivity is at a minimum, as shown in Figure 3. Mechanical properties are adequate for most applications, and economics are usually most favorable. Where greater structural strength is required, higher densities are called for, as shown in Figures 4 and 5. An additional benefit of higher density is reduced water vapor permeability, as shown in Figure 6.

Both the insulation thickness and the foam density employed affect the cost of the insulation material. A 2 pcf foam applied to a thickness of 2 inches requires as much material per square foot of insulated surface as a 4 pcf foam applied to a thickness of 1 inch. These two factors can be combined in the density-thickness factor, expressed in (pounds per cubic foot) (inches) or pcf-inches, and illustrated in Figure 7.

THE METHOD OF APPLICATION

The advantages in application presented by spray-applied rigid polyurethane foam are based on two distinctive characteristics: its light weight, and its ability to adhere to almost any surface. When one considers that this excellent insulation weighs, on an equivalent volume basis, only one-fifth as much as cellular glass or silicate, it is understandable that good adhesion renders sprayed foam self-supporting, entirely eliminating the need for supporting devices such as clips, straps, and bands. The monolithic nature of the insulation eliminates the need for multiple layers, staggered joints, joint adhesive, and reinforcing mesh. No other insulation of significance can be spray applied with such ease and with such dramatic cost savings.

Because of the speed with which rigid polyurethane foam can be spray applied, many insulation jobs that would have previously involved man-days of labor can now be completed in man-hours. The cost savings on labor alone can be dramatic, particularly on large tanks that are relatively free of obstructions.

The factors affecting application rates and application labor costs deserve careful consideration. The first factor is the maximum capacity of the spray gun used. A low capacity spray gun could restrict application rate if the spray crew is slowed down by the inability of the spray gun to insulate the area which could be covered by crew movement at a reasonable speed. On the other hand, excessively high capacity can be superfluous and even detrimental to product quality if the crew has difficulty keeping up with the spray gun.

The second factor is the degree of utilization. A crew working its way through scaffolding around a still column, for example, may spend more time moving equipment and hoses than actually spraying. A crew mounted on a boom to insulate the sides of a large field storage tank would be actually spraying a greater percentage of the time than the same crew working on a small vessel in the crowded quarters of a chemical processing

unit, stopping frequently to get around piping and instrumentation, and to put protective covering on gages and flange bolts. High winds could temporarily halt outdoor spraying. The effect of these two factors on effective application rate is shown in Figure 8.

The third factor is the density-thickness factor, a combination of two factors as discussed in an earlier paragraph. The greater the amount of material required per square foot of surface to be insulated, the greater the amount of time required to cover that surface with a given capacity. This effect is illustrated in Figure 9.

The fourth factor is the crew labor cost. A three-man crew would obviously cost more per hour than a two-man crew. If the third man, however, operated a boom so that the two-man crew actually spraying could operate without scaffolding, the resulting increase in application rate could produce a lower application labor cost per square foot insulated. These effects are illustrated in Figure 10.

CONDITIONS OF SERVICE

Some of the service temperatures involved in industrial insulation are presented in Table 1. The field of industrial insulation can be arbitrarily divided into three temperature

regions; the temperature region from 0°C. to 125°C. is designated as the moderate temperature region, temperatures below 0°C. are in the low temperature region, and temperatures above 125°C. are in the high temperature region.

The moderate temperature region presents perhaps the least problems because the temperature of service is close to the temperature of application and to ambient temperatures. Both temperature differentials and temperature changes tend to be small. It is in this region that many vessels have hitherto operated without insulation because the heat savings did not justify the use of costly insulation; it is also in this region that many storage vessels fail, and field storage tanks present perhaps the greatest opportunity for savings through reduced application costs.

Performance characteristics in the moderate temperature region have been extensively studied (6,17). The major problems are dimensional change and increase in thermal conductivity. In the absence or failure of effective barriers, air and water vapor enter from the surroundings under the influence of their respective partial pressure gradients, while the urethane polymer effectively inhibits the movement

of fluorocarbon. There is a tendency for the foam to expand through creep as the internal pressure in the foam cells increases, and a tendency for thermal conductivity to increase as the fluorocarbon is diluted with air and water vapor. Laboratory aging of thin, unprotected specimens can give alarming changes in dimensions (7,10) and thermal conductivity (6,10,14). Spray-applied rigid polyurethane foam, however, remains subject to the substrate as long as adhesion is maintained, and dimensional changes due to aging and to differences in expansion coefficients are almost non-existent under such conditions. The rate of change of K-factor is reduced by the presence of an impermeable substrate on one side and a protective coating on the other.

In the low temperature region, the problem of liquid oxygen compatibility eliminates most foam formulations from use at temperatures below -180°C . At such low temperatures, in the absence or failure of effective barriers, air entering from surroundings is condensed; because of the difference in boiling points between oxygen and nitrogen, fractionation occurs and results in oxygen enrichment of the condensed phase within the foam. Detonation may occur upon impact, the probability of detonation being a function of force of impact, liquid oxygen concentration, and chemical composition of the foam (12,13,18).

1257
100
X

At temperatures above -180°C . in the low temperature region, the major problem is moisture accumulation. In the absence or failure of an effective barrier, water vapor entering from the surroundings condenses and freezes, increasing the thermal conductivity of the foam (14). The water vapor permeability of rigid polyurethane foam is a function of its chemical and physical structure, and can, within certain limits, be controlled by formulation (3,9). Increasing foam thickness to prolong service life can in certain cases be more economical than using an expensive vapor barrier.

In the high temperature region, thermal degradation is the limiting factor, as discussed in an earlier paragraph. Where the extent of degradation approaches a limiting value at a given distance from the hot surface, increasing the insulation thickness by this amount can give satisfactory service. Performance is extremely dependent on chemical and physical structure.

The fire protection aspect is an important factor in industrial insulation, since some insulation materials provide a measure of protection in the event of fire, and are preferred for this reason. Rigid polyurethane foam is an organic material and will decompose if the temperature is high enough. At a high

enough temperature and in the presence of sufficient oxygen, either these materials or their decomposition products will burn. Apparent fire resistance as measured by a flammability test is dependent on the severity of exposure (11). A good spray applied foam will ignite when exposed to a fire but will not contribute significantly to it or its spread. Until some degree of protection is proven, however, rigid polyurethane foam cannot and should not be relied upon to provide fire protection. The hazard should be evaluated and safety relief valves and vents on equipment should be sized accordingly.

THE PROGRAM

Because polyurethane foam technology has shown rapid development during recent years, materials that are representative of current technology have not been in actual service for long periods. Most published case histories of spray-applied rigid polyurethane foam insulation involve periods less than six years (1,4,5). Even a service life limited to this period of experience, however, can justify its use if sufficient savings are obtained. Where periodic shutdowns are routine, or where reinsulation does not necessitate a costly shutdown, an insulation system that costs

2
3
4

one-half as much as another needs to last only one-half as long to offer a cost advantage based purely on investment cost, performance characteristics being equal.

The case studies listed in Table 2 are spray foam insulation applications conducted at the Institute and South Charleston Plants of Union Carbide Corporation, to develop technology and acquire experience in the use of this insulation material. Only applications in the moderate and high temperature range are discussed in this paper, since the development of satisfactory vapor barrier systems for the low temperature range from $-180^{\circ}\text{C}.$ to $0^{\circ}\text{C}.$ lies largely in the area of coatings technology.

Two types of spray foam formulations were used, a general purpose spray system that was considered satisfactory at temperatures up to $125^{\circ}\text{C}.$, and experimental spray systems that were proposed for higher temperatures. The general purpose spray system was a commercially marketed material that was ordered from stock. The experimental spray systems were designed on the basis of the most advanced technology available at the time, for specific case studies, and prepared in drum quantities for direct field application.

The use of the experimental spray systems was carefully monitored, with research and development and engineering experts participating as consultants on aspects such as fire protection, and plant engineers providing design data and information on operating conditions.

Fire protection precautions included the use of a fire retardant weather barrier coating, and attention to water spray protection and relief valve size. The nature of the chemicals involved was taken into consideration; rigid polyurethane foam was not used on equipment handling unstable flammables such as ethylene oxide, acetylene, and peracetic acid, or products near their auto-ignition temperature, and rarely used on aluminum equipment.

Personnel protection measures were developed and improved during the course of the program. For outdoor application, safety goggles, hard hat, and a fresh-air mask covering mouth and nostrils were finally recommended. For indoor application, a fresh-air mask covering the full face was required.

RESULTS

The most striking result of the program was the dramatic cost savings achieved with spray-applied rigid polyurethane foam. The actual insulation costs were based on the actual

material and labor expended on the job, making full provision for overhead expenses. The costs of equivalent conventional insulation, applied according to existing thermal insulation specifications, were estimated using standard cost estimate factors developed through experience with conventional insulation methods.

On many individual jobs, the cost savings exceeded 50 per cent of the cost of conventional insulation. This limited program alone saved over \$50,000 in insulation costs.

As expected, application rates were significantly higher with buildings and large storage tanks than with process vessels in crowded quarters. The time required to move from one job site to another was reduced by providing a wooden platform, later replaced by a trailer, which accomodated the entire spray unit and the drums of resin and activator.

Actual field experience developed application technology which could not be obtained from laboratory work. Spray applications under adverse weather conditions such as rain, wind, and snow flurries were successfully completed

using techniques such as enclosing the scaffolding with plastic, use of drum heaters and electrical tracing on hoses, partial frothing with dichlorodifluoromethane, and steam heating of process equipment.

Surface preparation ranged from none, through wire-brushing and sand-blasting, to painting. Untreated surfaces included mill scale as received, and previously applied and sometimes weathered paint. Good adhesion to some decidedly dirty surfaces was achieved, but this is not recommended practice. The final surface preparation recommendations called only for dry surfaces clean of scale, dirt, oil and grease, and for protective coating of stainless steel.

Because spray-applied rigid polyurethane foam tends to adhere to almost any surface it strikes, techniques had to be developed to minimize overspray and protect items such as flange bolts and instruments which had to be kept free of insulation.

Because rigid polyurethane foam expands over thirty-fold in the process of foaming, spray foam application techniques are much more critical than would be the case in spray painting. Application personnel rapidly acquired the skill necessary to produce final surfaces that were acceptable from an esthetic viewpoint.

Continued exposure of uncoated foam to sunlight resulted in ultraviolet degradation, and an opaque coating was found to be necessary. The foam was also susceptible to solvent attack by some chemicals under certain conditions, and severe damage resulted in one case from the discharge of hot solvent from a relief vent which was inadvertently directed at the foam.

CONCLUSIONS

The use of spray-applied rigid polyurethane foam as a thermal insulation material offers substantial cost savings when judiciously used. It is clearly the most economical insulation system in cases where it is suitable for use.

ACKNOWLEDGEMENT

The author expresses his appreciation to W. R. Proops and W. N. Stoops, under whose guidance and encouragement this work was done; to D. R. Richardson and E. C. Shipley, without whose initiative and support this work would not have been possible; to E. C. Burford, who supervised the field application work and improved application techniques; to W. A. Burnette and L. L. Jones, who assisted in gathering information and scheduling applications; to W. C. Turner, who provided his valuable experience on insulation materials and techniques; to P. E. Burgess, Jr., W. C. Kuryla, and

R. W. McLaughlin, whose competence and imagination produced the experimental systems used; to P. D. Berry, W. H. Rankin, and W. M. Sinclair, who developed the general purpose system; to J. J. Walker and D. H. Way, who investigated the fire protection aspects; and to J. L. Barker and L. S. Vandelinder, who investigated the corrosion protection aspects.

REFERENCES

- (1) Abbott, R. A., and Robertson, E. J., "Spray Application of Rigid Urethane Foams", SPE Journal 18, No. 5, 561-567 (May 1962)
- (2) Backus, J. K., Darr, W. C., Gemeinhardt, P. G., and Saunders, J. H., "Thermal Decomposition of Rigid Urethane Foam", J. Cellular Plastics 1, No. 1, (January 1965)
- (3) Barringer, C. M., "Designing Rigid Urethane Foams for Low Moisture Permeability", SPE Journal 15, 961-965 (November 1959)
- (4) Below, E., "Insulation from a Spray Gun", American Painter and Decorator (June 1961)

- (5) Gerhart, H. L., "Protective Coatings", Ind. & Eng. Chem. 57, No. 8 (August 1965)
- (6) Harding, R. H., "Relationships between Cell Structure and Rigid Foam Properties", J. Cellular Plastics 1 (July 1965)
- (7) Harding, R. H., and Hilado, C. J., "An Investigation of Some Dimensional Stability Tests Applied to Rigid Cellular Plastics", 7th Annual Technical Conference, SPI Cellular Plastics Division (1963)
- (8) Harding, R. H., and Hilado, C. J., "Some Relationships Among Strength, Temperature, and Chemical/Physical Structures in Rigid Urethane Foams", J. Appl. Polymer Sci. 8, 2445-2460 (1964)
- (9) Hilado, C. J., and Harding, R. H., "Some Relationships Between Water Vapor Permeability and Chemical/Physical Structure in Rigid Urethane Foams", J. Appl. Polymer Sci. 7, 1775-1790 (1963)
- (10) Hilado, C. J., "Effect of Accelerated and Environmental Aging on Rigid Polyurethane Foam", 1966 Polymer Conference Series, Wayne State University (May 1966)

- (11) Hilado, C. J., "The Flammability Characteristics of Cellular Plastics", 1967 Polymer Conference Series, Wayne State University (May 1967)

- (12) Key, C. F., and Riehl, W. A., "Compatibility of Materials with Liquid Oxygen", NASA MTP-P&VE-M-63-14 (December 1963)

- (13) Key, C. F., "Compatibility of Materials with Liquid Oxygen", NASA TM-X-53052 (May 1964)

- (14) Levy, M. M., "Moisture Vapor Transmission and Its Effect on Thermal Efficiency of Foam Plastics", J. Cellular Plastics 2, (January 1966)

- (15) Saunders, J. H., and Backus, J. K., "Thermal Degradation and Flammability of Urethane Polymers", Rubber Chem. & Tech. 39, No. 2, 461-479 (March 1966)

- (16) Smith, C. H., "Thermal Characteristics of Some Rigid Urethane Foams", J. Appl. Polymer Sci. 9, 3851-3861 (1965)

- (17) Stengard, R. A., "Properties of Rigid Urethane Foams", DuPont Bulletin (June 1963)

- (18) Thayer, R. M., Union Carbide Corporation, private communication (December 1966)

TABLE I. SERVICE TEMPERATURES IN INDUSTRIAL INSULATION

-268.9°C.	boiling point of helium
-252.8°C.	boiling point of hydrogen
-195.8°C.	boiling point of nitrogen
-183.0°C.	boiling point of oxygen
-161.5°C.	boiling point of methane
-103.7°C.	boiling point of ethylene
- 88.6°C.	boiling point of ethane
- 47.7°C.	boiling point of propylene
- 42.1°C.	boiling point of propane
- 34.1°C.	boiling point of chlorine
- 33.4°C.	boiling point of ammonia
- 19.2°C.	boiling point of formaldehyde
- 4.4°C.	boiling point of 1,3-butadiene
0°C.	freezing point of water
24.1°C.	boiling point of trichlorofluoromethane
34.0°C.	boiling point of propylene oxide
56.1°C.	boiling point of acetone
80.1°C.	boiling point of benzene
100°C.	boiling point of water
107.9°C.	boiling point of isobutanol
110.6°C.	boiling point of toluene
125.7°C.	boiling point of octane
138.4°C.	boiling point of p-xylene
140.8°C.	boiling point of propionic acid
145.1°C.	boiling point of xylene
147.6°C.	50 psig saturated steam
160.0°C.	75 psig saturated steam
169.9°C.	100 psig saturated steam
181.8°C.	boiling point of phenol
187.3°C.	boiling point of propylene glycol
197.5°C.	boiling point of ethylene glycol
197.7°C.	200 psig saturated steam
231.2°C.	400 psig saturated steam
288°C.	boiling point of 1-naphthol
290.4°C.	boiling point of glycerol

TABLE II. CASE STUDIES OF SPRAY-APPLIED RIGID POLYURETHANE
FOAM INSULATION

<u>Case Number</u>	<u>Vessel or Structure</u>	<u>Foam System (S-standard, X-experimental)</u>	<u>Operating Temperature °C.</u>
1	storage tank, 10,000 gal.	S	15
2	chiller	S	
3	storage tank	S	
4	storage tank, 35,000-gal.	S	18-20
5	storage tank, 35,000-gal.	S	18-20
6	storage tank, 40,000-gal.	S	10
7	tank	S	
8	tank	S	
9	vending machine building	S	---
10	vending machine building	S	---
11	vending machine building	S	---
12	vending machine building	S	---
13	vending machine building	S	---
14	shipping building	S	---
15	still column, top section	X	192-227
16	still column, top section	X	110-175
17	converter	S	100
18	storage tank	S	35-95
19	storage tank	S	35-95
20	transformer building	S	---
21	instrument building	S	---
22	evaporator	X	175
23	evaporator	X	175
24	reactor	X	
25	still column	X	
26	still column	X	
27	storage tank, 6,000-gal.	S	40
28	storage tank, 20,000-gal.	S	20
29	storage tank, 20,000-gal.	S	20
30	storage tank, 20,000-gal.	S	20
31	storage tank, 20,000-gal.	S	20
32	storage tank, 1,000-gal.	S	40
33	storage tank, 500-gal.	S	5
34	storage tank	S	
35	storage tank, bottom section	S	
36	building	S	---
37	still column, top section	S	-30-0
38	storage tank, 18,000-gal.	S	
39	heat exchanger	X	
40	scrubber	X	
41	make tank	X	
42	hopper, steam-traced	X	50-165
43	tank	S	
44	storage tank	S	
45	storage tank	S	---
46	storage tank, 30,000-gal.	S	---
47	storage tank, 30,000-gal.	S	---
48	storage tank, 40,000-gal.	S	---
49	storage tank, 40,000-gal.	S	---
50	still column, top section	S	-30-0

FIGURE 1. APPROXIMATE EFFECT OF TEMPERATURE ON THERMAL CONDUCTIVITY
OF ISOTROPIC 2 PCF TRICHLOROFLUOROMETHANE-BLOWN RIGID
POLYURETHANE FOAM.

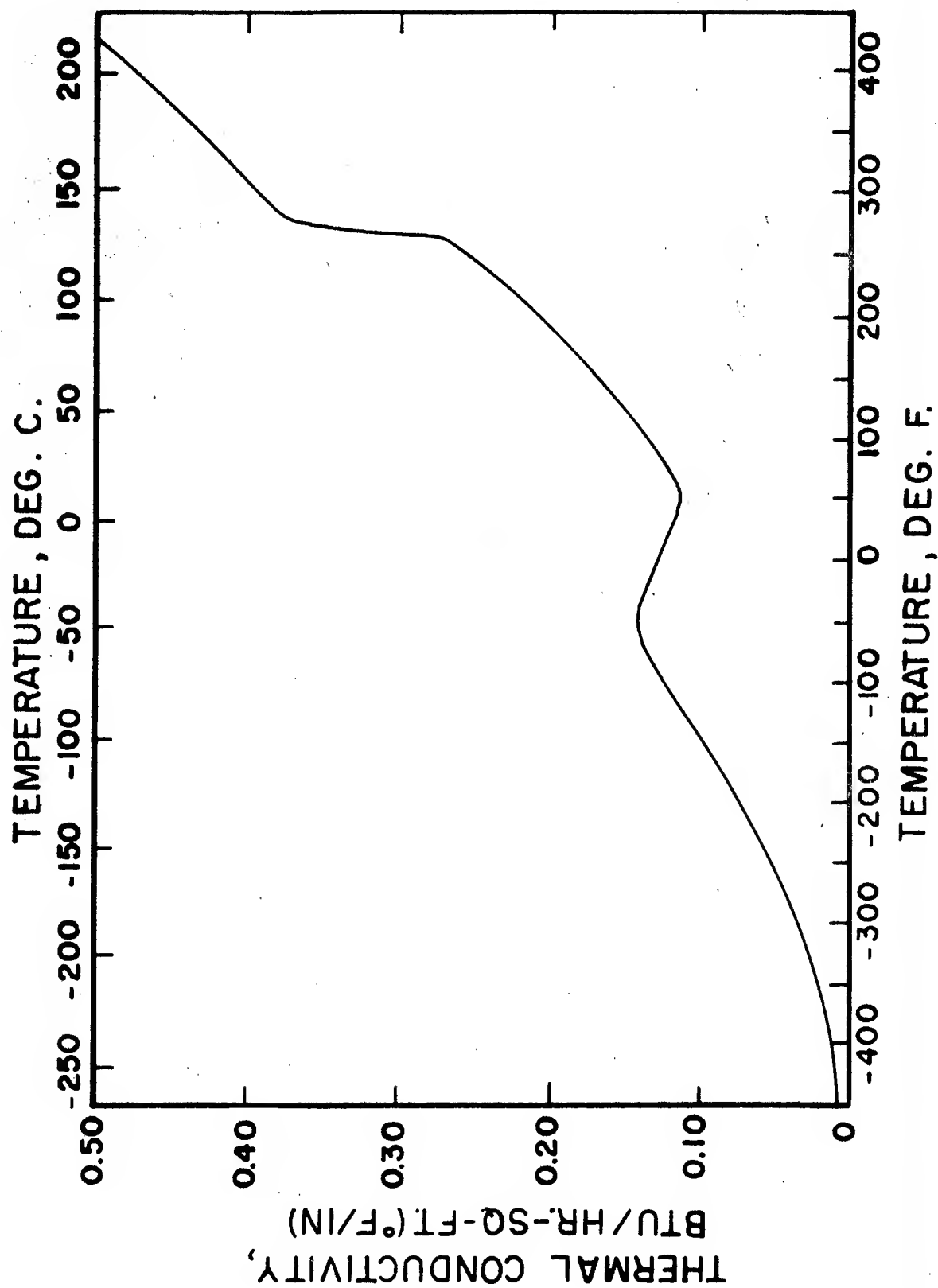


FIGURE 2. APPROXIMATE EFFECT OF TEMPERATURE ON MECHANICAL PROPERTIES OF ISOTROPIC 2 PCF TRICHLOROFLUOROMETHANE-BLOWN RIGID POLYURETHANE FOAM.

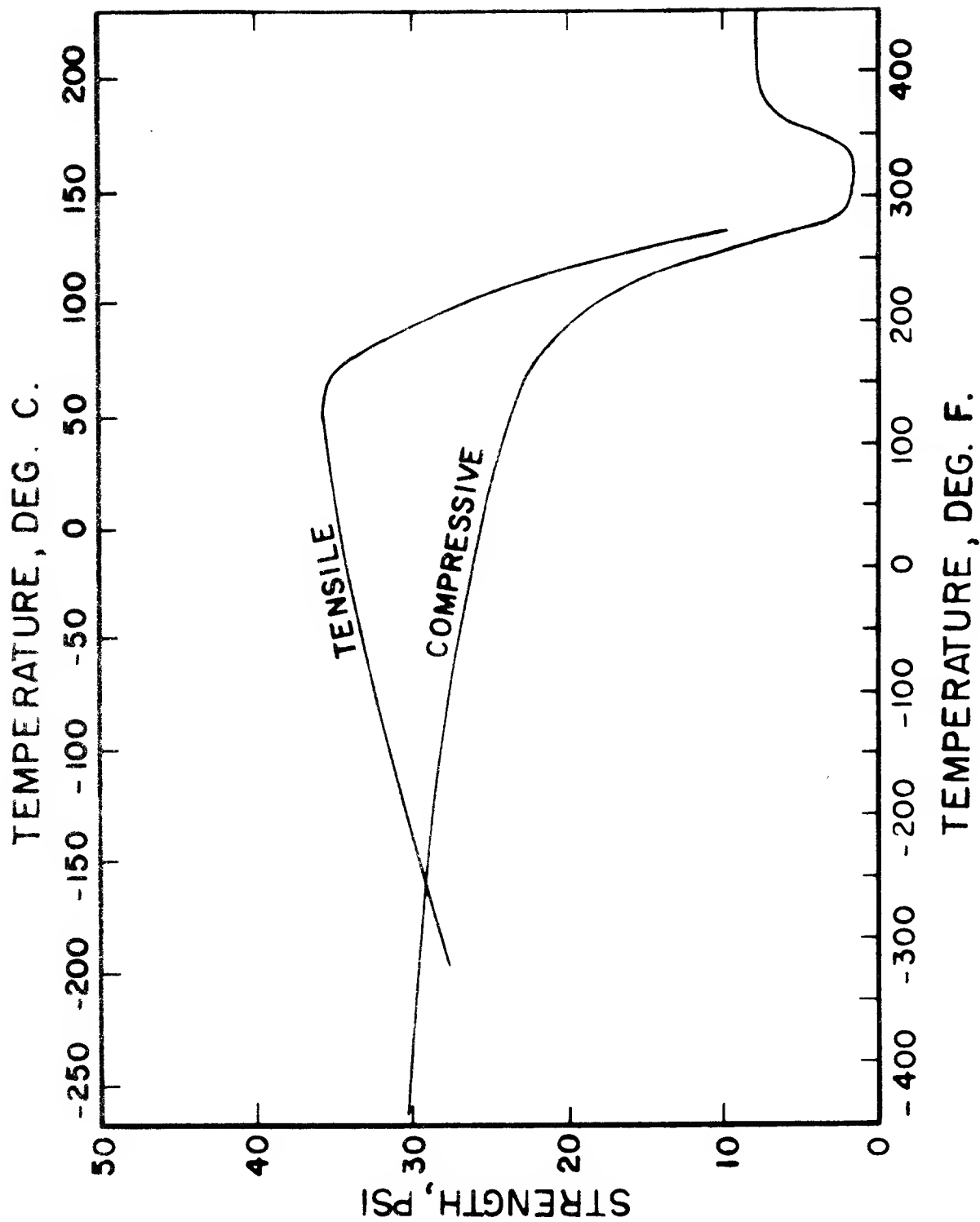


FIGURE 3. APPROXIMATE EFFECT OF DENSITY ON THERMAL CONDUCTIVITY OF ISOTROPIC TRICHLOROFLUOROMETHANE-BLOWN RIGID POLYURETHANE FOAM.

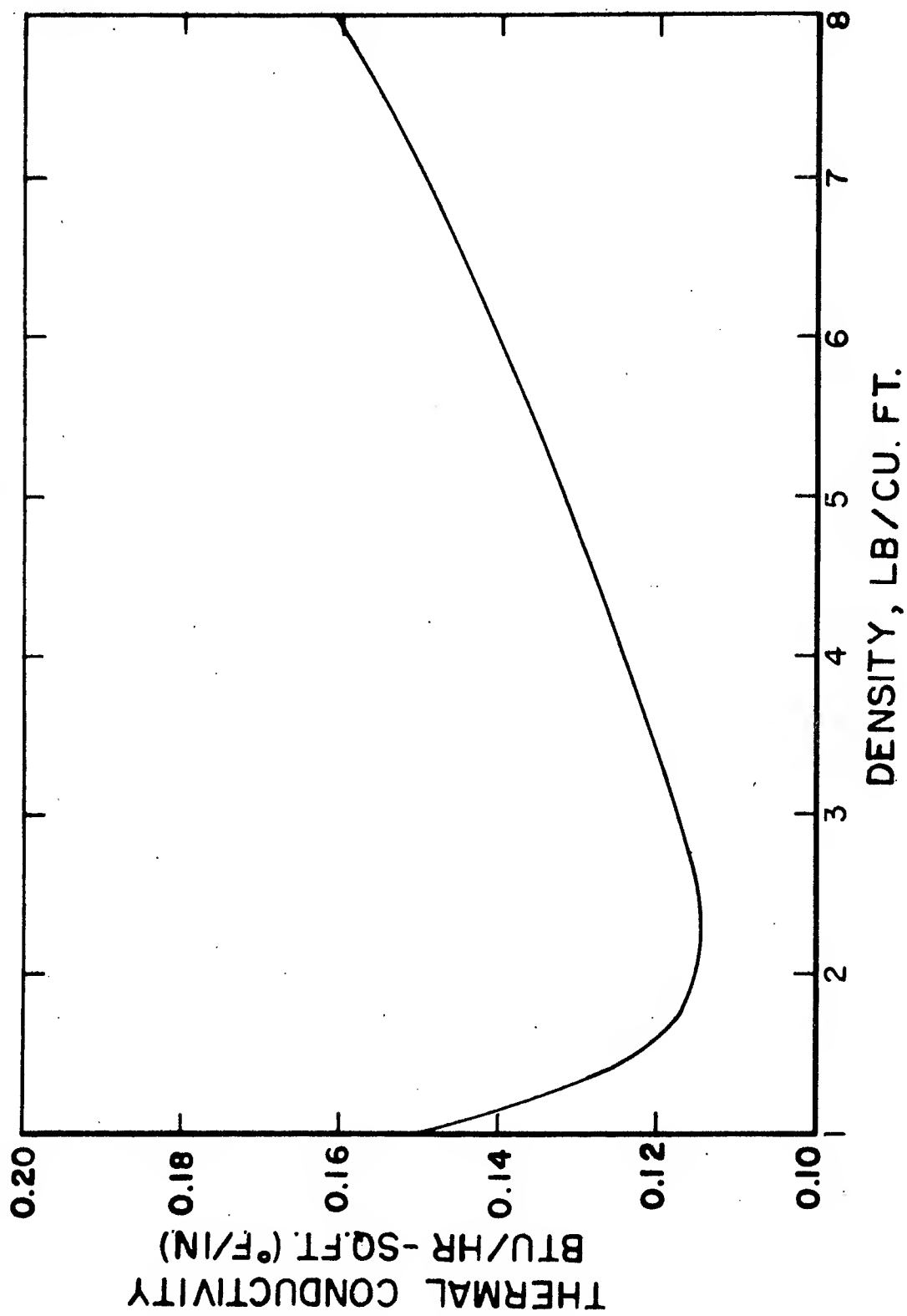


FIGURE 4. APPROXIMATE EFFECT OF DENSITY ON MECHANICAL STRENGTH OF ISOTROPIC TRICHLOROFLUOROMETHANE-BLOWN RIGID POLYURETHANE FOAM.

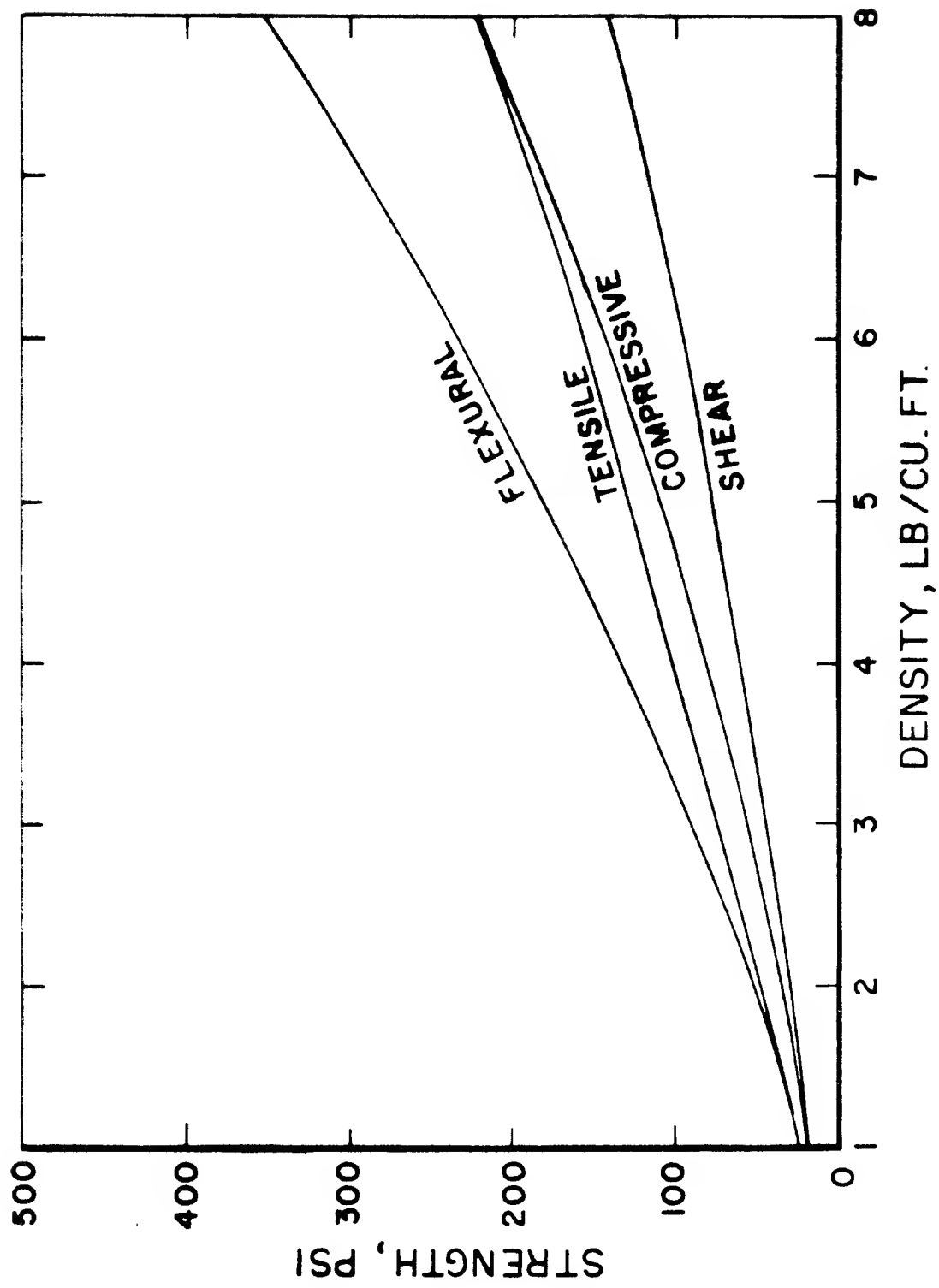


FIGURE 5. APPROXIMATE EFFECT OF DENSITY ON MODULUS OF ISOTROPIC TRICHLOROFLUOROMETHANE-BLOWN RIGID POLYURETHANE FOAM.

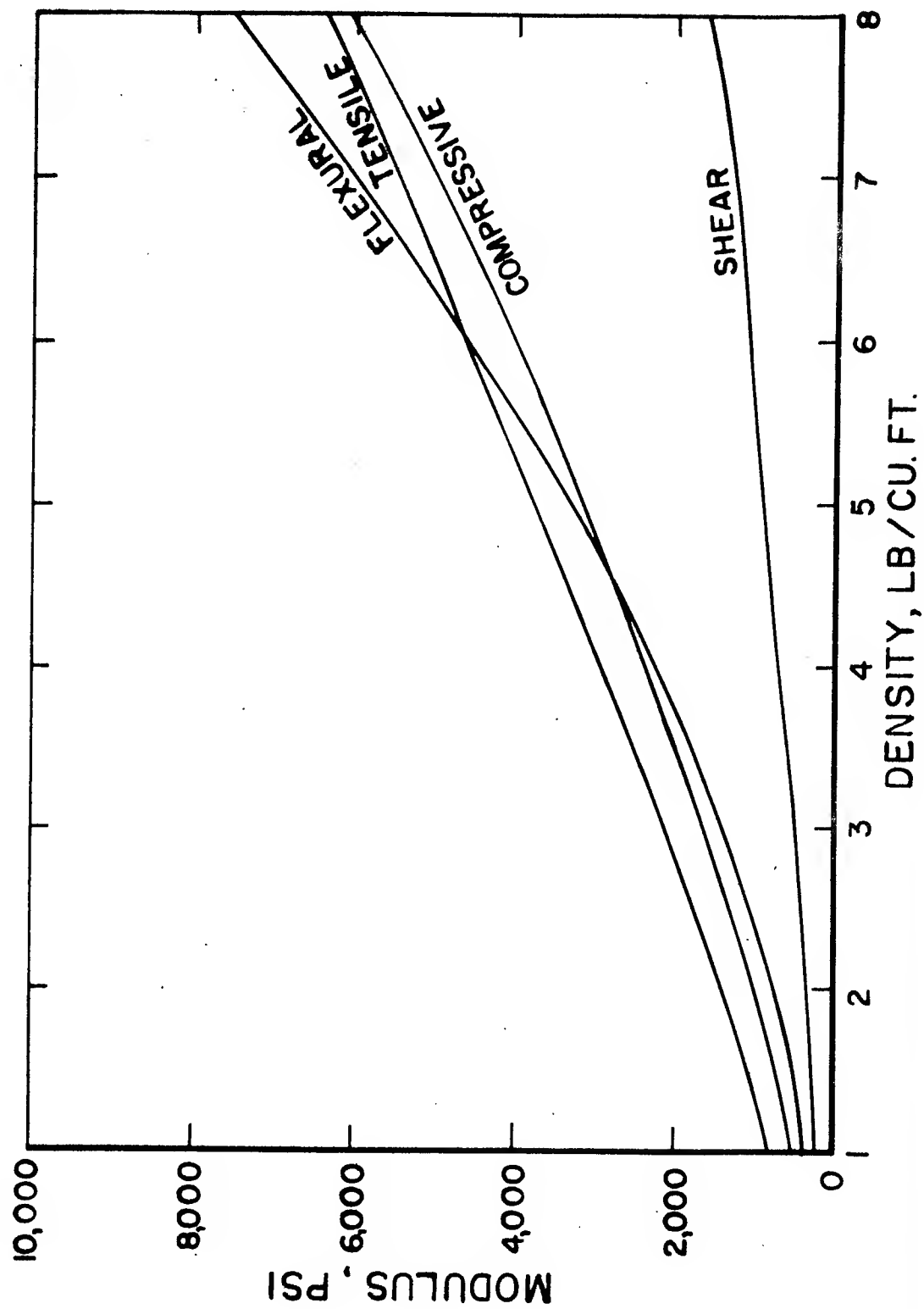


FIGURE 6. APPROXIMATE EFFECT OF DENSITY ON WATER VAPOR PERMEABILITY
OF ISOTROPIC TRICHLOROFLUOROMETHANE-BLOWN RIGID
POLYURETHANE FOAM

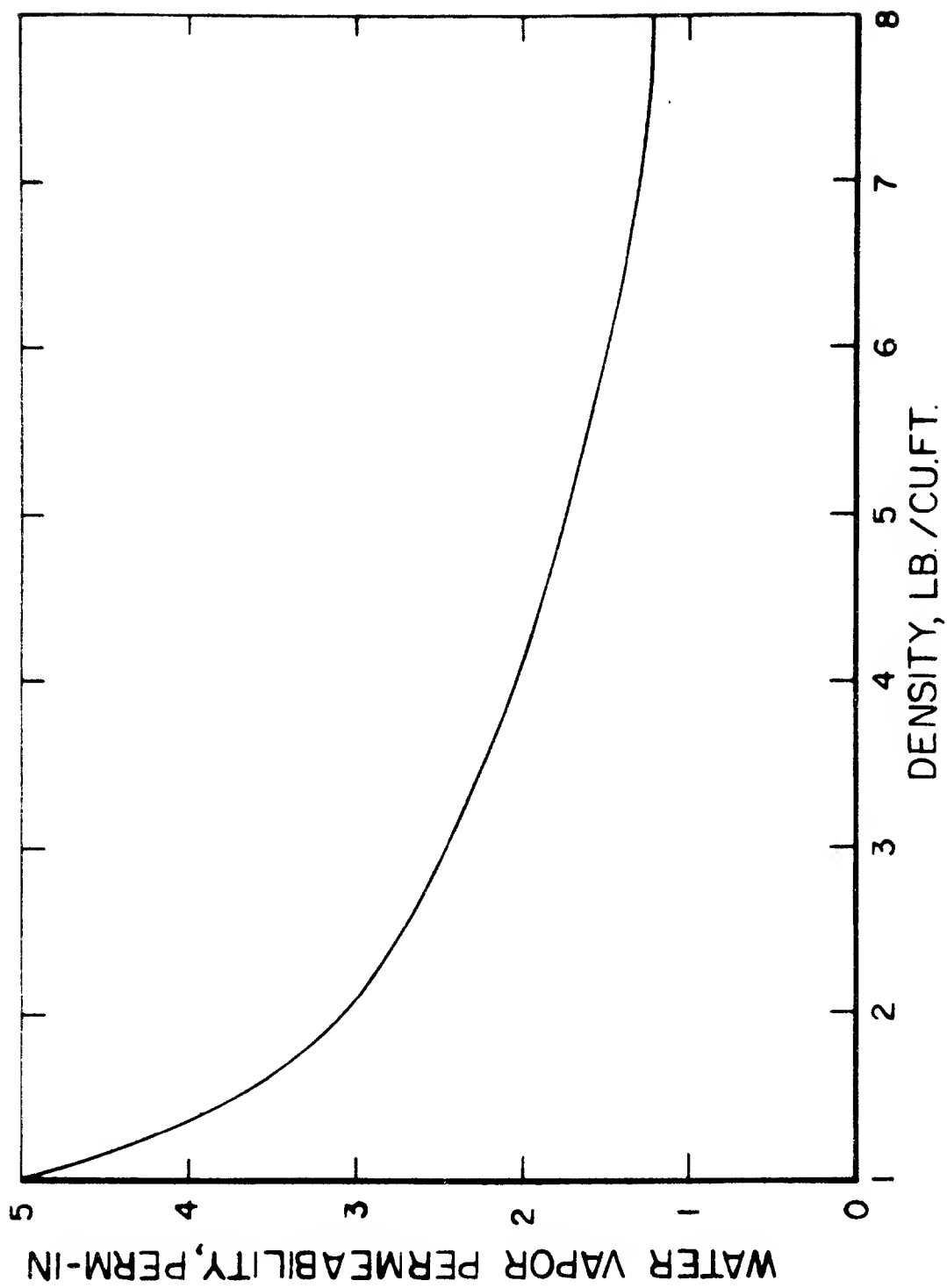


FIGURE 7. EFFECT OF DENSITY-THICKNESS FACTOR AND FOAM SYSTEM COST ON INSULATION MATERIAL COST (EXCLUSIVE OF SURFACE PREPARATION, APPLICATION, AND COATING COSTS)

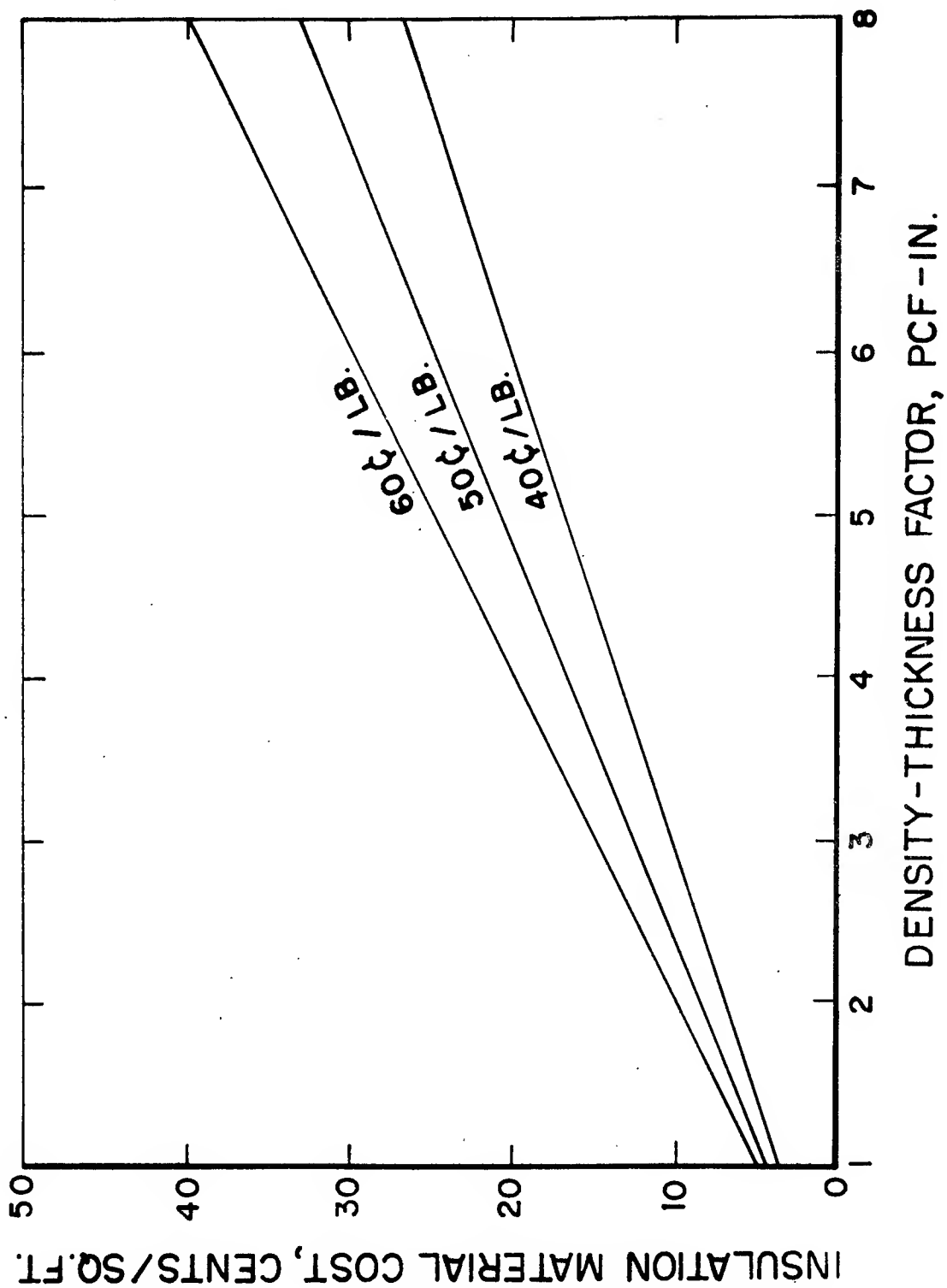


FIGURE 10. EFFECT OF SPRAY GUN CAPACITY ON THE UTILIZATION OF
APPLICATION RATE

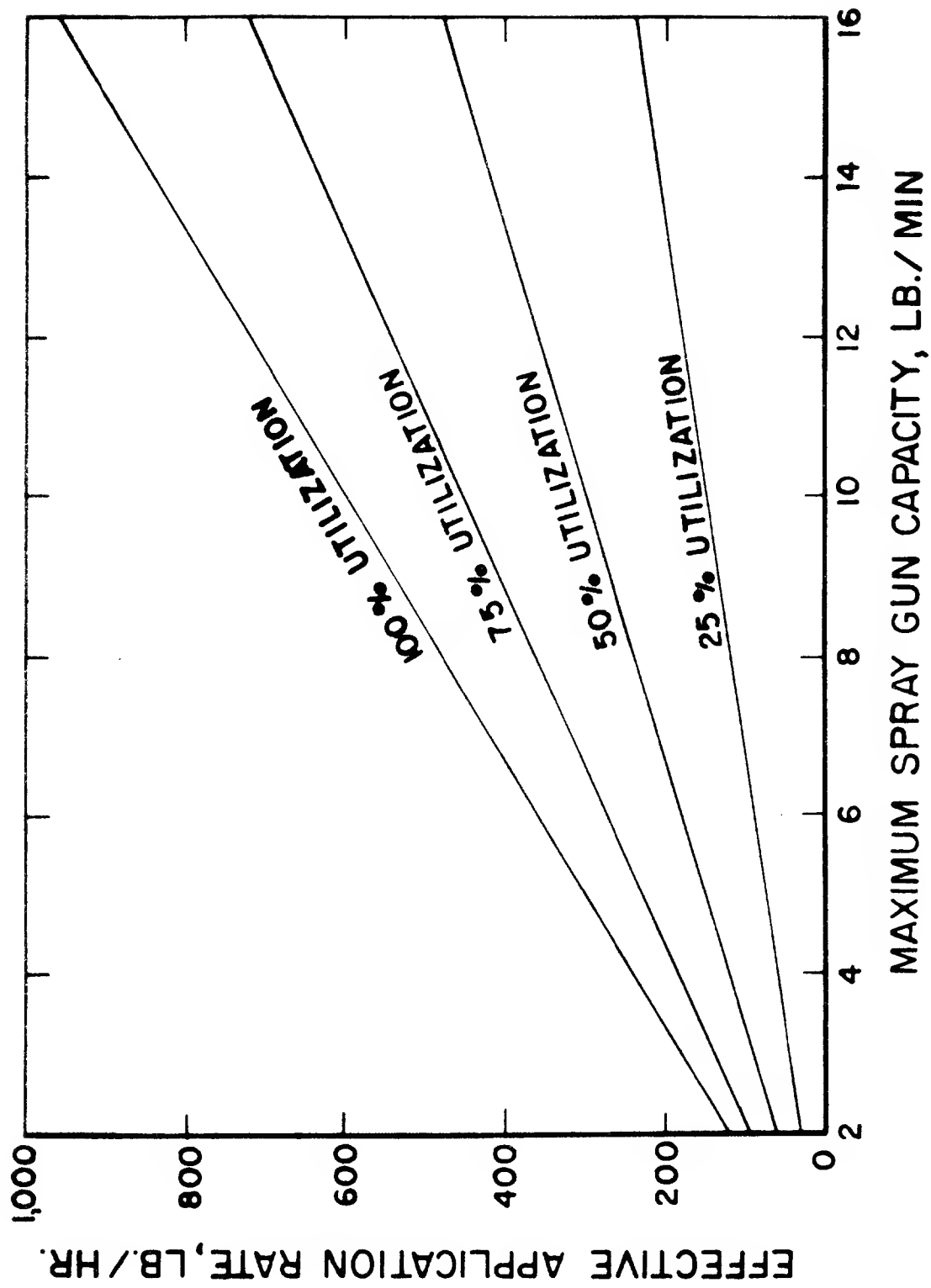


FIGURE 9. EFFECT OF APPLICATION RATE AND DENSITY-THICKNESS FACTOR ON INSULATION RATE

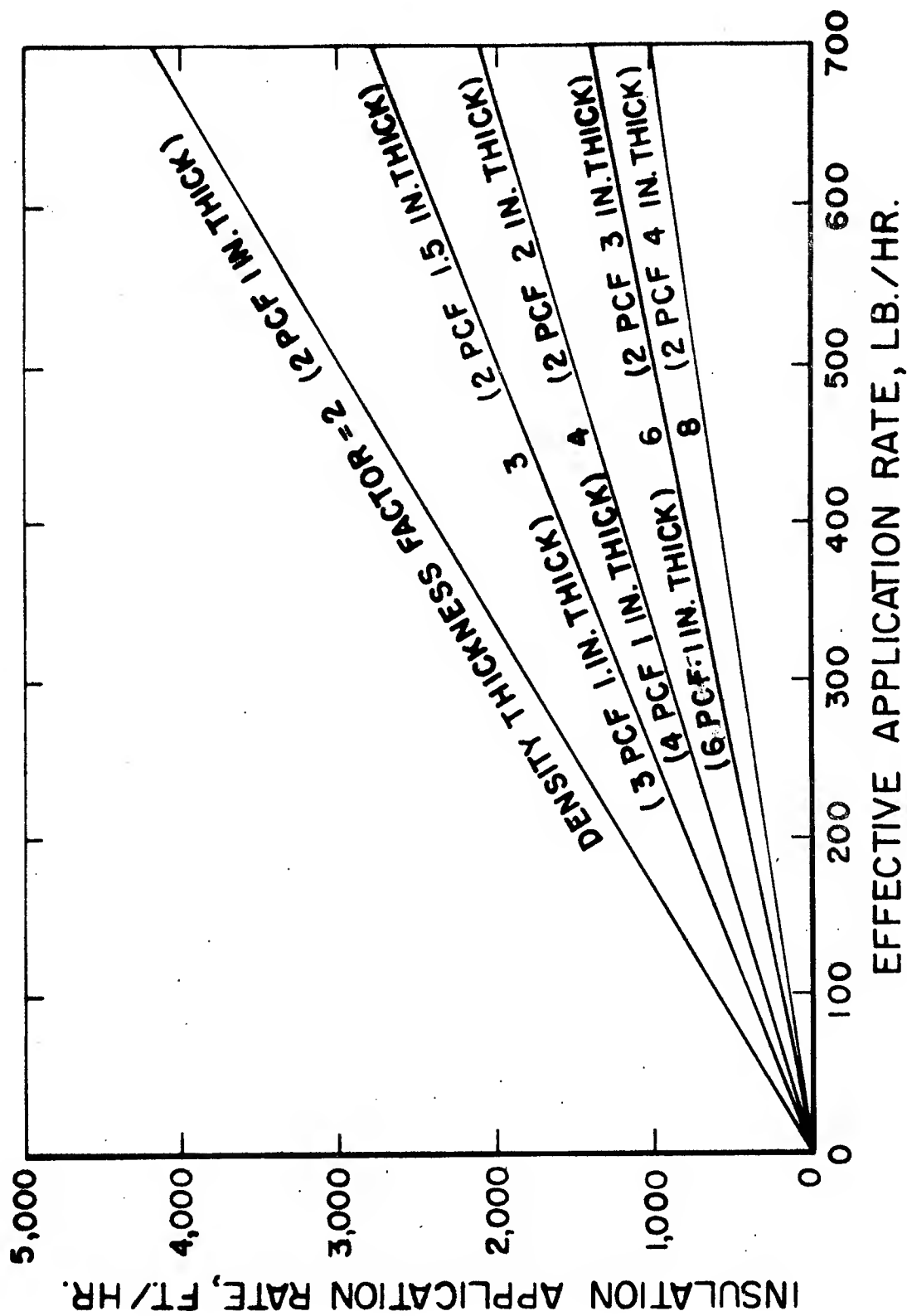
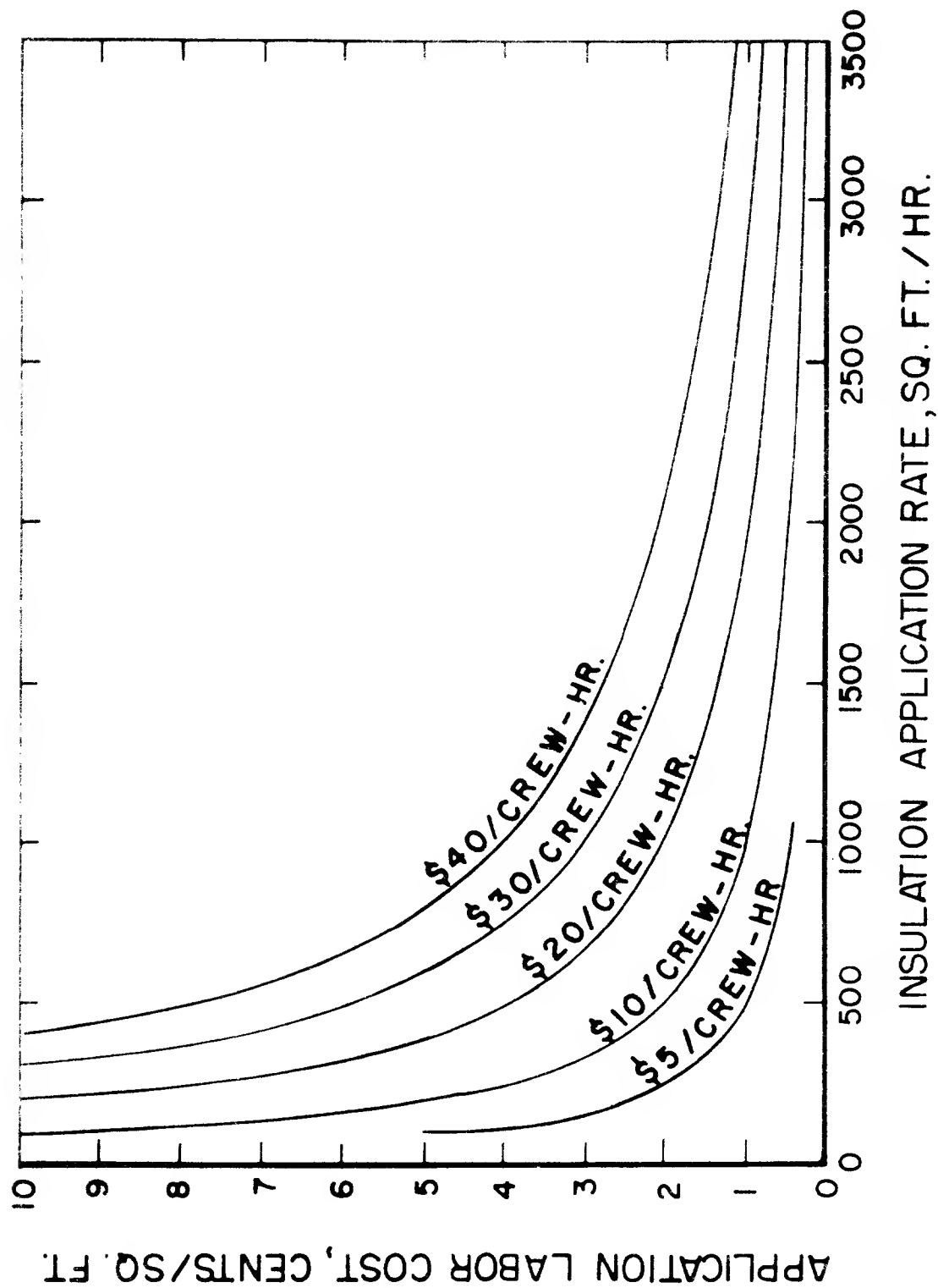


FIGURE 10. EFFECT OF INSULATION RATE AND CREW LABOR COST ON APPLICATION LABOR COST



10214-04

POLYETHYLENE FOAM I -
MODIFIED PE FOAM SYSTEMS

BY

Dr. Calvin J. Benning

W. R. GRACE & COMPANY
WASHINGTON RESEARCH CENTER
JUNE, 1966

POLYETHYLENE FOAM I. MODIFIED PE FOAM SYSTEMS

by

Dr. C. J. Benning

I. INTRODUCTION

There are two major areas of commercial application of polyethylene foams, medium density PE foams (22 to 35 pcf.), used predominately as electrical wire insulation and low density PE foams (2 to 8 pcf.), prepared as planks and logs, for buoyancy applications.⁽¹⁾ Other applications for PE foams are in packaging, gasketing, and construction industries. In these last three end-use areas, PE foam has not made as large an impact on the market as polystyrene foam because of the following reasons: First - packaging applications demand high modulus foams for container rigidity and good shock absorbing properties to protect material during handling. Second - foams must possess good resiliency and low creep for gasket applications, to minimize cold flow and compression set. Third - the construction industry demands load-bearing and insulating properties of the foam, in addition to low cost and non-flammability.

At the present time it is difficult to prepare polyethylene foams in the same price range as polystyrene foams. High modulus, low density, uniform cell structure and low cost make polystyrene an excellent foam. However, polyethylene has one inherent advantage over other materials. The physical properties can be varied over wide limits.

One of the main drawbacks of unmodified low density polyethylene foams is the poor resistance to creep. These are; PE foams made by extrusion which have closed cells and are prepared by either physical expansion of gases or volatile liquids or by chemical decomposition of gas releasing agents. One can modify the cushioning characteristics of the foam by rupturing the cells and changing the cell structure.

Skochdopole and Ruben⁽¹⁾ (See Figure 1), have described the change in compression-deflection when one punctures the cells.

The compression behavior is altered by this process, however, there is no change in long term aging; and in many cases the tensile properties and creep behavior of the foam deteriorate.

The cushioning properties of low density PE foam have been compared⁽¹⁾ with the properties of some typical foams, namely, polystyrene and foamed latex. These are illustrated in Figure 2. The compression-deflection curves illustrated in Figure 2 show the wide range of properties one can obtain from a low modulus, low density foam rubber to a high modulus polystyrene foam.

It would be ideal if one could take a simple system (i.e. polyethylene) and vary its properties from a very flexible rubber-like foam to a rigid foam. This is an ideal situation that we are always trying to develop. The cost/performance of polyethylene and the ability to modify its chemical structure make it commercially and technically attractive.

Theoretically, polyethylene is an ideal system because; (a) inter-molecular attraction is low (absence of non-carbon hydrogen bonding) and can be controlled by crosslinking, and (b) new polymer systems can be developed by grafting several different polymer structures together. These methods, therefore, allow us to modify the chemical structure according to set patterns. Figure 3 illustrates how this has been done with several complex mixtures. The diagram also shows how one can produce soft, flexible rubber-like foams and rigid foams by changing the composition of the polymer system.

Articles have been written that describe the preparation of PE foams. Henry Lasman,⁽²⁾ discussed foam preparation and use of blowing agents, and their use in the compression molding of low density foam. Foams used in wire coating applications and prepared by extrusion were discussed by Ralph Hansen of the Bell Laboratories in several of his papers.^(3,4)

This paper describes a method for regulating foam properties by crosslinking and grafting polymer blends during the foaming process using organic peroxides. We will concentrate on the preparation of foams by compression molding. We will discuss the process and

how it influences foam structure and mechanical properties. We will also discuss the preparation of foams of desired physical properties and will translate polymer properties into foam properties. Finally, we will describe the application of these techniques to multi-component mixtures.

II. PROCESS DESCRIPTIONS

Foamed wire coating is made by extruding a mixture of polyolefin with blowing agents and nucleating agents under optimum extrusion conditions to produce small cells at high efficiency.⁽³⁾ It is essential that the blowing agent have the decomposition characteristics compatible with the time, temperature requirements of the specific polymer system and the process. Uniform distribution of components in the composite is required. The Visco-elastic properties of the polymer as it leaves the extruder and expands must be controlled to trap the maximum amount of gas without undue restriction. The system must withstand large high speed deformations without brittle failure. In the compression molding process this is accomplished by crosslinking. A method used to modify the properties of wire insulation, is to cure foams after expansion in conventional rubber curing apparatus. This allows more freedom to operate under different conditions and improves the mechanical properties of the foamed insulating materials.

Low density PE foams, used as life preservers, sealants and gaskets are made by the expansion of low density PE with volatile components (i.e. fluorocarbon or hydrocarbon) directly by extrusion. Similar extrusion processes have been developed overseas for producing PE foamed sheet of low density by (6 pcf. - 0.1 gm/cc) controlling the extrusion process. Foams in the form of film, tubing, planks, bats and sheet have been made by regulating mixtures of polymer, blowing agents and extrusion conditions.

However, low density PE foams (3-4 pcf.) have not been made with balanced properties and low creep. Compression molding allows one to vary the mechanical properties of the foams by changing polymeric compositions. The compression molding process for preparing foamed polyolefins can be summarized as follows:

The process consists of: First - the resin (or resins), modifiers, blowing agent and crosslinking agent are mixed in a Banbury or similar intensive mixer. Second - the molten mass is transferred to a preheated mold and molded at high pressure until the mixture is cured and most of the blowing agent is decomposed. Third - the pressure is released, thus allowing the mixture to expand freely at atmospheric pressure.

We have accomplished several objectives by using peroxide initiated, grafted, crosslinked polymer systems. Foams of excellent cell structure (1 to 2 mil cell diameter) have been made from a variety of resins and blends. Both elastomeric and rigid foams have been made by modifying the composition of the graft. We have determined the scope and limitations of the compression molding process and find it to be a very versatile tool in evaluating new resins and foaming systems. A better understanding of the foaming mechanism can be obtained and this in turn used further to obtain additional information involving new formulations and continuous foaming techniques.

III. EFFECT OF PROCESS VARIABLES ON FOAM PROPERTIES

As we said previously, compression molded foams have superior physical properties because of smaller cells, uniformity of structure, and the cured state of the resin.

Figure 4 illustrates how crosslinked PE makes a more stable creep resistant system. (7)

The compression molding process we are discussing consists essentially of three steps: (1) Intensive mixing above the melting point to insure uniform dispersion of additives, (2) Molding at high pressure to control cell structure and uniformity and (3) expansion.

The intensive mixing cycle is one of the most important variables in the process. Time, temperature and rate of shear must be regulated to insure optimum dispersion without premature crosslinking or expansion. If the blowing agent decomposes prematurely then the material expands in the Banbury, thus making uniform molding impossible. If the melt crosslinks prematurely, the polymer mass will not fill the mold or

expand uniformly without seams and splits. The stability and concentration of blowing agent and curing agent are therefore, important parameters.

In the second step the molten mixture is transferred from the Banbury to a preheated mold and cured under pressure. This technique improves heat transfer and restricts premature expansion during the cure. Pressure is released when 90% of the expanding agent has decomposed, and the resin has reached the maximum state of cure.

The cured object is ejected from the mold and is allowed to expand.

A. EFFECT OF PRESSURE

High pressure favors the formation of a super saturated solution of gas in the molten polymer while low pressures allow the gas to diffuse and agglomerate. Figure 5 shows how cell size can be changed by regulating pressure. The final density of the foam is not effected by molding pressure.

B. ROLE OF THE CROSSLINKING AGENT

Polyethylene does not have sufficient melt viscosity and elasticity above the melting point to absorb the shock of large deformations at the high speeds encountered during expansion. Curing agents (radiation and organic peroxides) increase the melt viscosity and elasticity to the desired level necessary to contain the gas in a uniform cellular structure during expansion.

In Figure 6 we have illustrated how the peroxide concentration and degree of cure effect foam stability. Higher molecular weight resins require less peroxide to produce a stable foam.

At a low degree of cure (<30% gel) gas is lost because the resin has poor high temperature extensibility, therefore, the expanded material ruptures and shrinks. Expansion is uniform between 40 and 70% gel. As the degree of cure increases, the melt elasticity increases and restricts expansion. This is described in Figure 7. Density increases with increasing degree of cure. The shaded area in Figure 7 represents 38

different polymer systems investigated.

In our previous work(6,7) we described the time-temperature-concentration requirements for processing polyethylene with several organic peroxides. Lupersol 130⁽⁸⁾, (2,5 dimethyl-2,5 di(tertiary butyl peroxy) hexyne) was the organic peroxide used in this study.

C. ROLL OF THE BLOWING AGENT

Azobisformamide, (ABFA), (the blowing agent used in this study) produces nitrogen, CO and CO₂ according to the equation given in Figure 8. The gases expand the resin and control the final density of the foam. Blowing agent should not decompose during the intensive mixing cycle of the process. In this study there was no loss of gas during molding or subsequent increase in density of the molded material. A super saturated solution of gas in the crosslinked polymer is produced during high pressure molding and curing. As pressure is released, gas on the surface of nucleating agents desorbs and expands the resin. Nucleating agents may consist of the peroxide or ABFA-decomposition residues, secondary polymer systems, low molecular weight fractions or foreign material that absorbs gas. Therefore, expansion occurs by diffusion and dissolution of gas. The expansion process is extremely rapid (<2 sec.) and three - dimensional. For example, molding a standard 1/2" x 10" diameter disc will yield a 1" x 19" or 20" diameter disc of 6 pcf. g/cc. Low density foams have been made at 2 1/2 pounds per cubic foot. As the density of the foam decreases such problems as mold design, heat transfer and specialized foam handling become more and more important. At these low densities we are dealing with materials that are extremely fragile at the molding temperature of 400°F.

We have restricted our studies to ABFA as a blowing agent for three reasons: (1) It produces a high yield of gas with a minimum discoloration and odor, (2) It is commercially available and FDA approved up to 2 wt. % and (3) The blowing agent doesn't interfere with crosslinking reaction.

IV. PHYSICAL PROPERTIES OF COMPRESSION MOLDED FOAMS

The physical and chemical properties of a foamed plastic are determined by the nature and composition of the solid and gas phases. The physical properties of the foams can be shown to be related to the following structural variables; density (concentration of solid and gas), cell structure, and polymer structure. A correlation between these variables and the physical properties has been established and will be described in the following sections. Cell structure (open or closed), cell size and polymer modulus are important in determining initial compression-deflection or cushioning behavior of foams, (Figure 1). The main differences in behavior at the low compression values described in this paper (5 to 25% deflection) are in the region where one would expect polymer structure to exert its major influence, (Figure 3) as long as the cell structure (the ratio of open/closed cells) remains essentially constant. Large variations in cushioning properties can be effected by changes in cell structure. Figure 9 shows two foams made of crosslinked 5 melt index, .95D ethylene-butene copolymer. Sample B was crosslinked prior to expansion and Sample A was crosslinked during expansion. Analysis has shown them to be identical in chemical structure. The only difference between the foams is the cell structure. Sample B is >95% closed cells 25 - 150 microns (1 - 6 mil) diameter and Sample A is >95% open cells 500 - 1000 micron cell (20 - 40 mil) diameter.

One may expect these curves to be reversed according to the data in the literature.⁽¹⁾ Close examination of the cell morphology shows that the struts at the cell wall junctions of Sample A are much heavier than B and more directional. During expansion cell windows were ruptured and/or melted into the strut section. The struts were then cross-linked after or during the final expansion.

Slight variations in compression-deflection behavior has also been noted with cells of various sizes. However, these differences are minor in relation to differences (See Figure 10) in polymer structure (Figure 3) and cell structure (Figure 9) the amount of open and closed cells.

A. DENSITY (WEIGHT/UNIT VALUE)

The effect of blowing agent concentration on foam density has been described in previous reports.⁽²⁾ Density decreases with increasing blowing agent concentration and is the main criteria for determining foam properties. Table I lists the physical properties of three different foams prepared from an experimental graft PE, a branched polyethylene and a linear PE. As the density decreases the foams become softer (lower modulus and lower compressive strength), see Figure 11. Tensile strength is directly proportional to the density because less polymer is present in the foamed composite.

B. CELL STRUCTURE

We have shown (in Figures 9 and 10) that the cell structure is extremely important in determining the stress-strain relationship of a foam under compression. Figure 5 shows the compression-deflection of foams prepared at decreasing pressure (4,000 psi to 180 psi) the average cell size increased as pressure decreases. Recent work reported at the 22nd. ANTEC of SPE⁽⁵⁾ shows that cell size of filled foams remains essentially constant over wide pressure ranges. This is presumably caused by absorption of gas by the filler. Changes in pressure are less noticeable in filled foams and multi-component systems.

C. FLEXURAL MODULUS

Flexural modulus is the standard test for determining stiffness. We have found that the modulus is a function both of the base resin and foam density (see Figure 11). It is independent of sample thickness and the preparative method. Table II list the modulus of a number of PE and modified PE foams. The modulus of the foams is much less than that of its solid counter-part. This limits the application of foams in many packaging areas. However, this limitation can be overcome by modifying the design by either making larger or thicker sections or by using ribs to stiffen the article. Foams are so much lighter that on the basis of equal weights they compare very favorably in their economics.

D. COMPRESSION-DEFLECTION

Compression-deflection describes the cushioning properties of the foam under load and is described as the amount of stress required to deflect a foam. Measurements were made at 5-10-25% deflection. The C-D values are effected by cell structure of the foams, for example, Figure 9 shows that the rate of change of deflection with increasing compressive force (stress-strain curve) is quite different for open cell foams and for closed cell foams of equivalent density. Figure 9 and 10 illustrate the compression-deflection (stress-strain curve) changes with cell size. C-D properties decrease with decreasing modulus of the parent polymer and have been illustrated in Figure 3. Decreasing the initial molecular weight of the resin also alters the C-D curve (Figure 12). These data illustrate how a cushioning material can be produced by the correct choice of resin system cell structure and density.

E. TENSILE PROPERTIES

The tensile properties are directly proportional to the foam density (see Table I) and tensile properties of the starting resin or blend. Table II lists the physical properties of compression molded foams of 8 lbs/cu. ft. density.

V. POLYMER PROPERTIES AND PHYSICAL PROPERTIES OF EXPANDED COMPOSITES

In the previous sections we have illustrated how the properties of a cellular plastic are determined by the two constituents in the composite, the gas and the resin system. As the volume of gas increases in the system (density-decreases) the gas becomes a dominant mechanical property regulator. This means that not only is concentration important (density) but also the uniformity and type of dispersion (cell structure). Below 8 lbs./ft³ the properties of the foam are more influenced by the gas phase. Therefore, investigations of the contribution due to the polymer phase must be conducted under closely controlled structural conditions.

We have controlled density, cell size and structure within narrow limits to determine how polymer properties effect foam properties.

Table I and II show that the compression, tensile and flexural modulus of a foam is directly proportional to that of the parent resin and its concentration in the matrix (density).

We have seen how crosslinking improves foam stability and polymer properties⁽⁷⁾. Frequently, small structural differences in two polymer systems is cancelled out by the crosslinking and foaming processes. Table III illustrates that the properties of the foam made from a linear ethylene homopolymer is within experimental error of one made from an ethylene-butene copolymer.

We have observed that higher degrees of cure produce a more uniform stronger foam.

In general, an increase in the molecular weight of the starting resin usually produces softer materials. Table IV shows that decreasing melt index from 5 to .2 results in a 50% decrease in modulus and lower compression-deflection values. Tensile strength is not effected.

VI. GRAFTED CROSSLINKED FOAMS

In many applications a combination of the favorable properties of different polymers is desired in a foam structure. For example, a low density polymeric cushioning material, inert to chemical attack, sterilizable and with good cushioning properties would be an attractive item of commerce, as a shoe insole, or as hospital bedding, crash pads, etc. Foamed PVC does not have the required compression-deflection behavior to make an ideal cushioning material. Polyolefins are chemically inert and easy to process, but low density polyethylene foams are not sufficiently stable at high temperature. The cell structure can not survive high temperatures and the foams are not thermally stable under normal operating conditions for cushioning in the automotive industry. Unmodified PE foams based on linear PE have the required thermal stability but do not have the cushioning properties necessary for comfort. Ethylene-propylene rubbers and other low modulus elastomers have the desired properties of cushioning but are difficult to foam and produce in a economical manner. If one could combine the favorable properties

of these resins then one could tailor-make foams by chemically combining several units together. Polyolefins have been modified by chemically crosslinking and grafting to other types of polymers. Modified olefin foams have been prepared by these techniques, with Lupersol-130⁽⁸⁾ as the curing agent.

There are several theoretical points to consider in our discussion: First - one must keep the crosslinked density (the degree of cure), the foam density and the molding conditions constant when we compare one system with another. Second - the choice of components will depend on several factors: (1) The mechanical properties desired, (2) Compatibility of the resins in the mixture, (two incompatible resins can not be expected to uniformly graft and crosslink to produce a foam having uniform properties in three directions); and (3) The stability of the resins toward thermal and free radical attack. This means that the reaction between polymers and free radicals must be completely predictable and the polymer mixtures must survive the high processing temperature necessary to "kick-off" the peroxide and blowing agent.

With these points in mind one can produce a variety of systems from various polyethylenes and grafted cross-linked systems having a very wide range of physical properties and can tailor-make foams to a specific application. High modulus materials can be made by using high modulus extruders and fillers. Low modulus materials can be made by combining rubber-like modifiers and other types of low modulus additives.

The following systems illustrate the versatility of the process.

A. POLYETHYLENE/ETHYLENE-VINYL ACETATE COPOLYMER BLENDS

Addition of ethylene-vinyl acetate copolymers to low density and high density polyethylene retarded the crosslinking reaction. Higher concentrations of peroxide were necessary to produce stable foams of equivalent structural integrity.

The graphs in Figure 13 show that stable uniform foams can be prepared from linear polyethylene (.96D, 5. Melt Index homopolymer) at 20-25% gel or 0.3 wt. % peroxide. Addition of 25 pts. of copolymer required a

minimum of 0.5 wt % peroxide or a gel level of 40% to produce uniform foams. Addition of 40 pts of copolymer completely disrupted the crosslinking and grafting reaction. 60/40 mixtures produced non-uniform foams with larger holes and fissures. Uniform foams of HDPE/EVAc mixtures can be made if EVAc concentration remains below 40 wt %.

Addition of ethylene-vinyl acetate copolymer to low density polyethylene had the same effects. Figure 13 shows how the curves have been shifted to the right. Although the crosslinking reaction is more efficient for LDPE, than HDPE. The addition of copolymer again retards the crosslinking reaction. Stable foams could not be prepared from 50/50 blends, however, excellent foams can be prepared from 75/25 and 85/15 blends. The mechanism of the crosslinking of PE-EVAc blends has been described elsewhere.⁽⁹⁾

Table V lists the properties of several typical foams. A comparison of the first two examples shows that a decrease in modulus and compression force is observed upon addition of the EVAc copolymer to polyethylene. Decreasing density, next three examples, causes the typical property changes observed in other systems. When the copolymer concentration is further increased (Run 4 and 5) the foams become softer.

In summary, the addition of EVAc copolymers to polyethylene requires additional curing agent to overcome the poor high temperature viscoelastic properties of the copolymer. Soft flexible foams, the C-D values of which approximate commercial cushioning materials can be made. The soft foams have very good cell structure and attractive C-D values.

B. LINEAR POLYETHYLENE (96D) AND BRANCHED POLYETHYLENE (915D) BLENDS

We have observed that preparation of low density foams (2 to 4 pcf.) from branched polyethylene is easier than preparing low density linear polyethylene foams. This has been attributed to the fast rate of crystallization observed with linear polyethylene and its poor melt elasticity. Combinations of branched PE and linear PE could be expected to retard crystallization and modify the rheology of the system.

Improvements in melt elasticity would also be predicted.

Blends of low and high density polyethylene were cured and expanded by compression molding. Table VI illustrates that a variety of stable foams can be prepared from these mixtures. Foams containing larger concentrations of linear PE have the expected increase in thermal stability. Figure 14 shows that blends containing higher concentrations of low density PE produced softer foams.

The properties of foams prepared from low density PE and polyethylene containing small amounts of butene comonomer (.95D) are graphically illustrated in Figure 14. The results are essentially the same as those in Table VI.

C. POLYISOBUTYLENE MODIFIED POLYETHYLENE FOAMS

We discussed previously that one of the major objectives of this research was to prepare foams with good stability. Another objective was to control the compressive properties, so that both a soft cushioning material and a rigid packaging material could be obtained with slight variations of the same process.

Linear PE foams have good thermal stability but poor cushioning properties. Addition of EVAc copolymers made softer foams but the thermal stability was lower than expected. The addition of rubbers could be expected to improve melt elasticity and lower compression-deflection response. Polyisobutylene (30 pts) together with 95D ethylene-butene copolymer (70 pts) was crosslinked and expanded. (Higher concentrations of PIB were difficult to process). Table VII lists typical foams made from the blend. As we expected, foams were softer and easier to process. The cross-linking reaction appeared unaffected by the PIB below 30 wt. %.

D. RUBBER MODIFIED PE FOAMS

Blends containing 10% elastomer were made with both .96D linear polyethylene and 95D ethylene-butene copolymer. Foams were unstable at higher elastomer concentrations and at low gel values (<30%). Cis-butadiene, butadiene-styrene copolymers and isoprene did not increase foam stability or melt elasticity.

Foams were softer as one would predict but the mixtures did not produce uniform foams like those made from the polyisobutylene modified systems.

E. EXPERIMENTAL POLYMERS (MODIFIED STRUCTURES)

Two experimental polymers were foamed using the compression-molding process. First - A special graft of linear polyethylene with a polar monomer (Gamma-resin) and Second - A linear polyethylene that had the terminal unsaturation converted to polar end groups. These two resins were expanded to illucidate the mechanism of crosslinking and expansions.

Gamma resin was easily foamed by the standard technique. Homogeneous foams were prepared at .3 wt % peroxide and 40% gel. Gamma foams were more rigid than low density PE and the polar monomer changed the crystallization characteristics sufficiently to produce softer foams than linear polyethylene products.

This system shows that one can graft two materials prior to crosslinking and expansion.

Polar polyethylene

The polar polymer crosslinked more rapidly than the standard (.96D ethylene homopolymer). However, the melt elasticity of the polar polymer was not sufficient to retain the gas upon rapid expansion. Uniform small celled foams could not be prepared by the standard compression molding techniques.

F. FILLED FOAMS

The general use of inorganic fillers in unfoamed PE has been reported⁽⁵⁾. The translation of these results to polyethylene foams is theoretically difficult. The behavior of thick unfoamed pieces must be translated to very thin sections, namely cell walls of the foam. We have described the foaming of crosslinked polymer and have shown how one can tailor-make a foam by choosing the correct polymer. There is one inherent weakness in the use of various curing systems to produce stable foams. The use of crosslinking agents unvariably reduces crystallinity of the parent resin and lowers the modulus. This produces softer foams. To increase the modulus of low density foam one must either use high modulus blends containing special polymer or filler.

The first alternative is expensive and involves certain processing limits. Fillers have been incorporated into crosslinked polyethylene foams and foamed blends to increase the modulus of the composite structure. (5)

SUMMARY

A process has been described for preparing modified PE foams with a wide spectrum of properties. Flexible polyethylene foams have been prepared by crosslinking and grafting blends of low modulus resins to PE prior to expansion. Flexible and semi-flexible foams have been prepared from crosslinked copolymers of ethylene with polar monomers, and blends of low density and high density PE. Rigid foams can be prepared by grafting high modulus resins to the polyethylene chain or by addition of fillers and extenders.

The molding process is described. The physical properties of PE foams have been shown to depend on the cell structure, polymer structure, and density. The interaction of these three main variables in the foamed composite are discussed and analyzed.

ACKNOWLEDGMENT

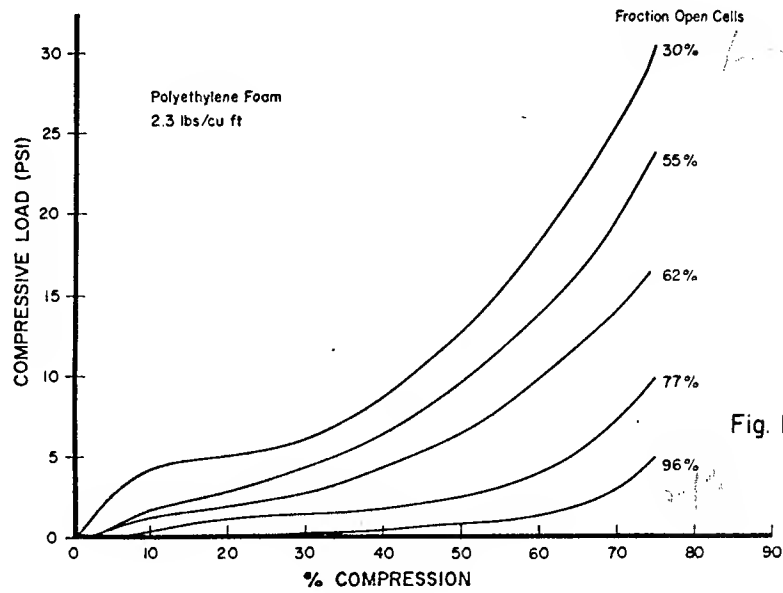
The mechanical properties were measured in the Physical Testing Laboratory at WRC of W. R. Grace and Company under the direction of Mr. G. E. Fulmer. The crosslinked and compression molded foams were made by Mr. R. L. Adams.

BIBLIOGRAPHY

1. Skochdopole, R. E. and Rubens, L. C., "Physical Property Modifications of L.D.P.E.", Modern Plastics, 1965.
2. Lasman, H. R., "Foaming Agents For Polyolefins", S.P.E. Journal, 18, 1184-91 (1962).
3. Hansen, R. H. and DeBenedicts, T., "Studies In The Decomposition Of Blowing Agents", A.C.S. Chicago Meeting, Div. Org. Coatings and Plast. Chem. 21, 2-32-7 (1961).
4. Hansen, R. H., "Production Of Fine Cells In The Extrusion Of Foams", S.P.E. Journal 1877-82 (1962).
5. Nutter, J. I. and Benning, C. J., "Filled PE Foams", Preprints 22nd. Annual Technical Conference, S.P.E., Montreal, Canada, March 7-11, 1966.
6. Benning, C. J., "Extrusion Of Peroxide-Containing Polyethylene", S.P.E. Journal 1083-1088 (1965).
7. Fulmer, G. E. and Benning, C. J., "Mechanical Properties Of Crosslinked Linear Polyethylene". Preprints 21st. Annual Technical Conference of S.P.E., Boston, Mass., March 1-4, 1965.
8. Wallace and Tierran "Product Bulletin" L-130.
9. Benning, C. J., Gregorian, R. S., Kirk, C. C., Werber, F. X., "A Continuous Process For Curing Tubing Of PE And PE Blends", 22nd. Annual Technical Conference S.P.E., Montreal, Canada, March 7-11, 1966.

Dr. Calvin J. Benning obtained his B.S. degree from the University of Notre Dame in 1950 and his Ph.D. from the Ohio State University in 1953. He joined the staff of the W. R. Grace Research Division in 1957. Before joining Grace, Dr. Benning was employed by M. W. Kellogg Co. as a senior research chemist. Prior to joining M. W. Kellogg he was employed by Hudson Foam Plastic Inc. His 12 years experience includes research, pilot plant and development of polyesters, polyurethane elastomers and foams, emulsion polymerization of fluorinated monomers, and synthesis of fluorinated polysulfides. His current interests are in plastic application and new product development. He is a member of SPE, SPI, AAAS, ACS and Phi Lambda Upsilon.

Compressive Load vs. Compression



① Load vs Compression for Plastic Foams

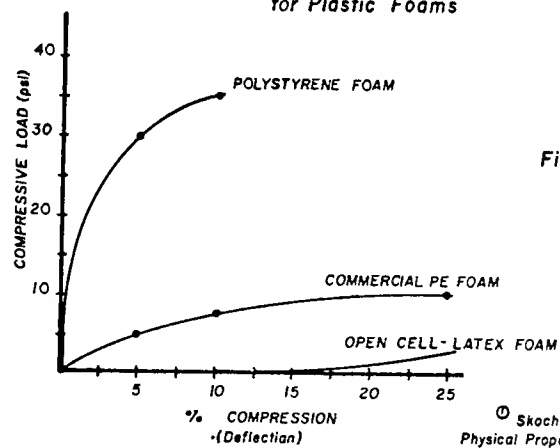


Fig. 2

① Skochdopole & Ruben
Physical Property Modifications of
Low Density PE Foams
Modern Plastics '65

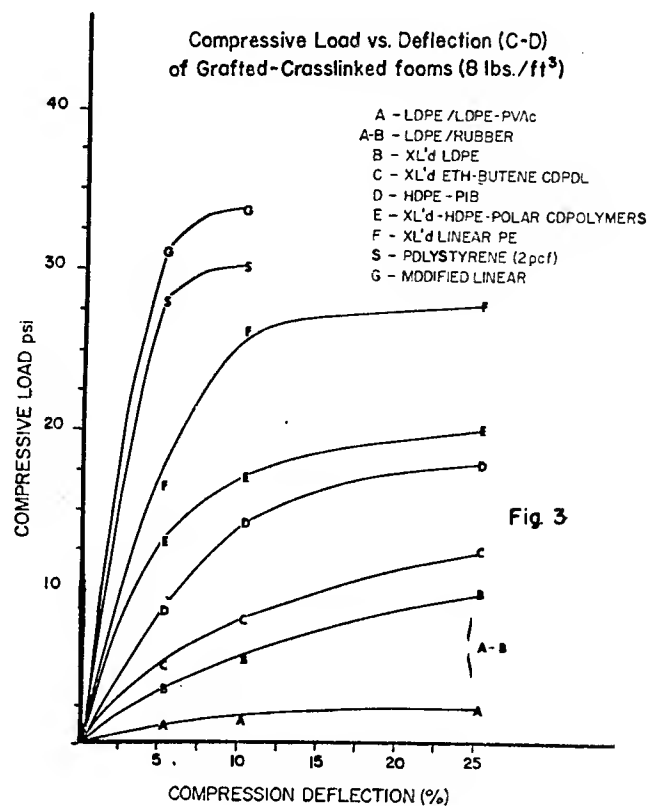


Fig. 4
Elongation vs. Gel Content IPSI 160°C 50-050C

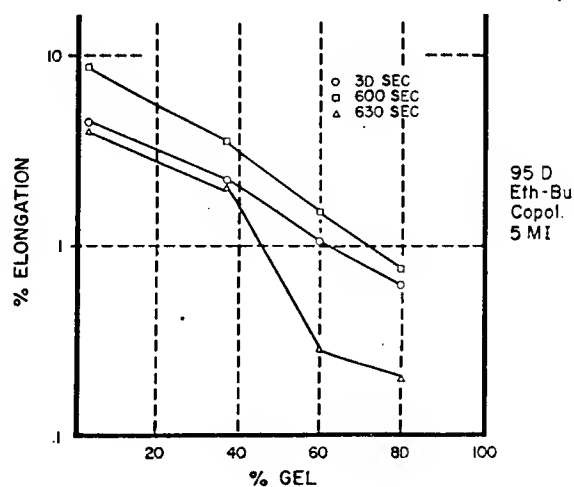
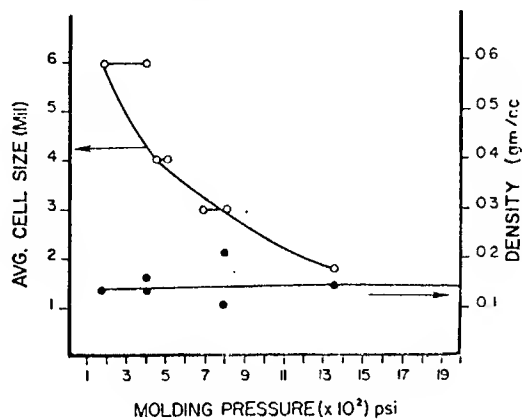


FIG. 5
Effect of Molding Pressure
on Cell Size and Density



Relationship between Peroxide Conc.,
Degree of Cure, and Foam Stability (Linear Polyethylene)

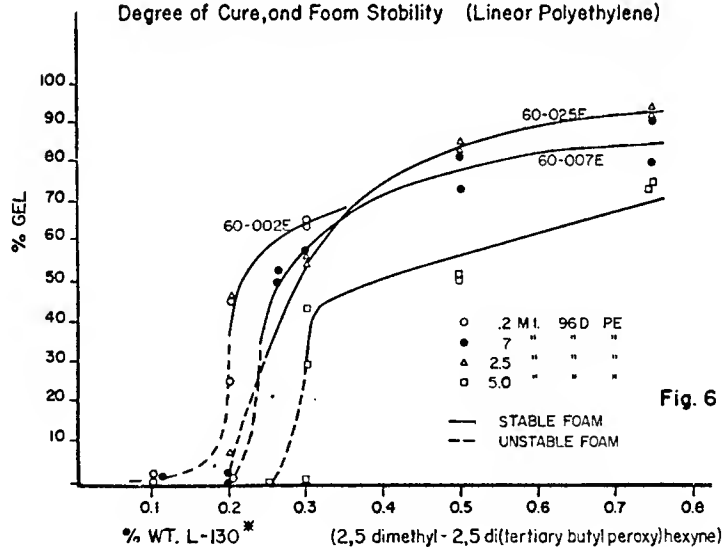
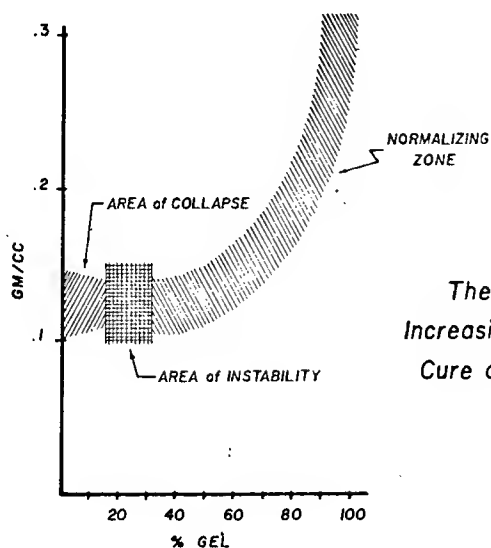


Fig. 6



The Effect of
Increasing Degree of
Cure on Density

Fig. 7

ABFA Equations

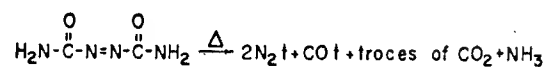
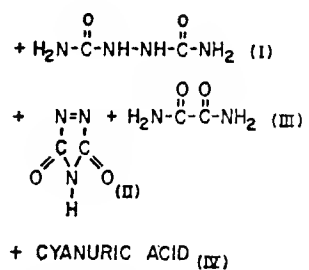


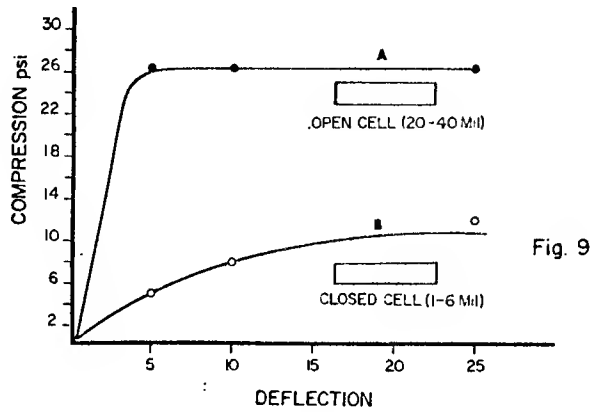
Fig. 8



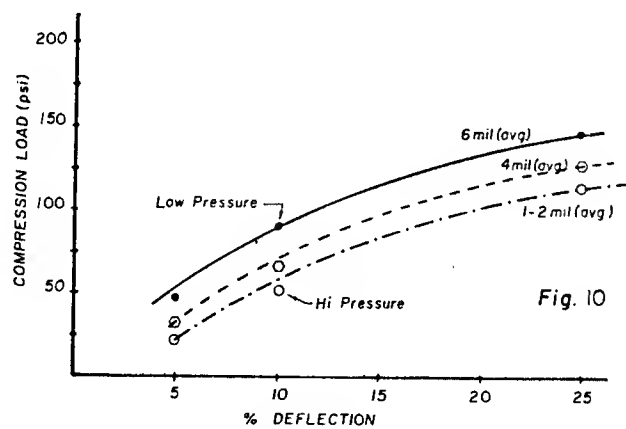
Analysis of the reactions shows the following:

- 230 ml gas (STP) is produced from 1g ABFA
- 66-68 % is residue composed of I, II, III, IV.
- Gases make up 32-33 % of original compound.
- These are 65 % N₂-33 % CO, 2 % CO₂ and traces of NH₃

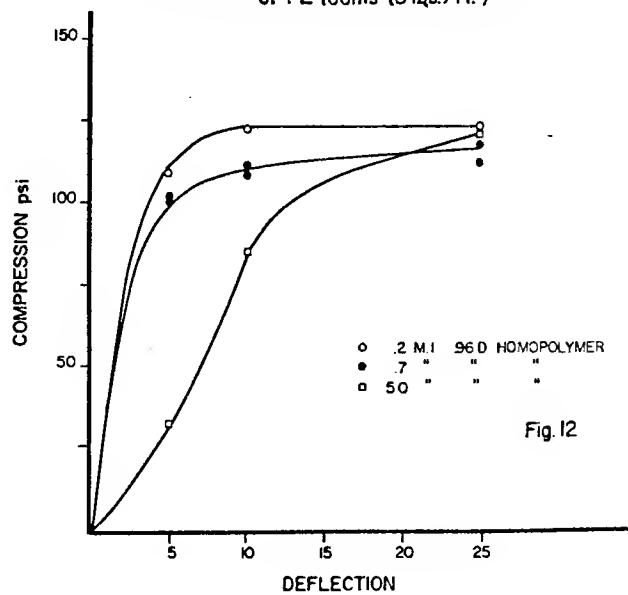
Effect of Cell Structure on Compression Deflection



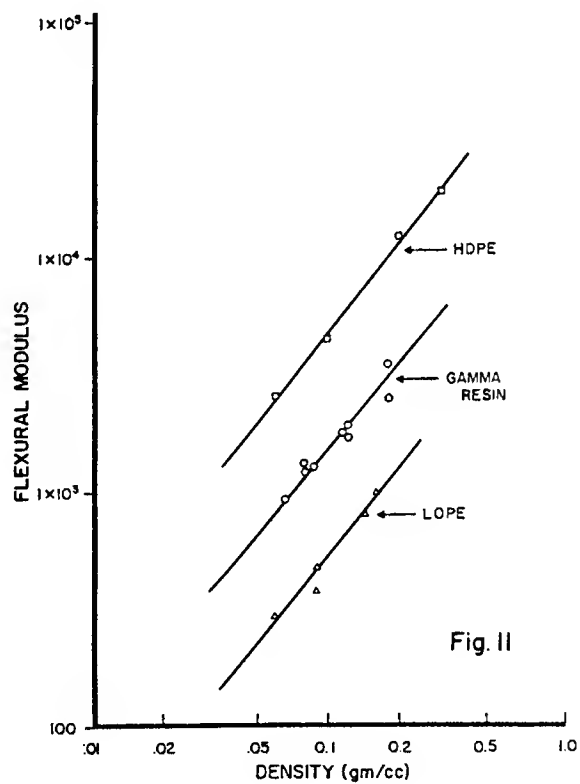
Effect of Cell Sizes On Compression Deflection



Effect of Melt Index on the Compression Deflection
of PE foams (8 lbs./ft.³)



Effect of Density on Flexural Modulus



Effect Of Ethylene Vinylacetate Copolymer On Crosslinking And Foam Stability

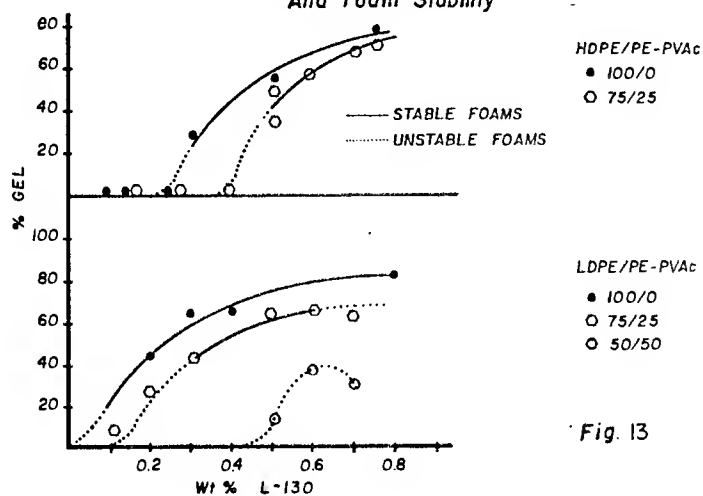


Fig. 13

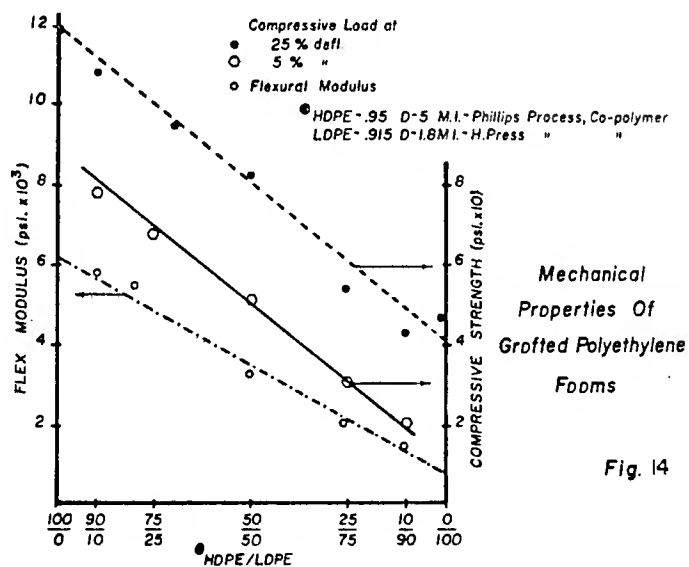


Fig. 14

TABLE I
EFFECT OF DENSITY ON FOAM PROPERTIES

Resin L.O.P.E.											
L-130 Conc.	ABFA Conc.	% Gel	Density (g/cc)	Cell Size (mil)	Flexural Modulus (psi)	Compression at			Tensile Properties		
						5%	10%	25%	Modulus psi	Strength psi	% Elong.
0.7	3	88	0.16	2	1,050	32	48	6.4	878	218	91
0.4		74	0.134	6	830	24	37	4.6	698	195	162
	6	72	0.087	3	380	5.5	10	14	620	124	113
	8	71	0.06	2	307	3.5	5.6	9	470	87	86
Polar Copolymer											
0.7	3	84	0.18	7	3,500	63	96	119			
0.3		41	0.12	5	1,750	27	44	51			
0.4	6	54	0.068	8	1,200	13	17	20	1,220	129	190
Linear PE .96D, 5.0 M. I.											
0.5	8	54	0.056	4.8	2,500	16	26	26	2,600	170	250
	4	54	0.099	3.7	4,400	54	67	73	3,700	210	220
	2	41	0.195	5	12,000	170	210	240	7,100	400	250
	1.5	62	0.29	10	19,700	220	290	430	23,600	700	210
	0.25	78	0.89		161,000	1,710	2,830	4,110	129,000	2,000	62

TABLE II
PHYSICAL PROPERTIES OF FOAMS BASED ON RESINS OF DIFFERENT STRUCTURE

Resin	96D - 5 MI	.950 - 5 MI	Polar Copolymer .1 MI	LDPE	LDPE/PE-PVAc
% Gel	52%	61%	61	74	72
Density (g/cc)	0.13	0.13	0.13	0.135	0.13
Cell Size - mil	3-4	2-3	8.8	5.7	4.7
Flexural Mod. - psi	6,800	6,500	1,967	830	580
Comp. Defl. at .5%	108	101	26	24	18
.10%	122	116	40	37	25
.25%	120	122	48	46	31
Tensile Mod. - psi	6900	5700	1941	698	567
Tensile St. - psi	250	260	193	195	165
Elong. at Failure, %	178	180	253	162	174

TABLE III

MECHANICAL PROPERTIES OF CROSSLINKED 95D and 96D PE FOAMS

Resin System	60-050E(1)	50-050C(2)
Formulation	.75% L-130(3) 3% ABPA(4)	.5% L-130(3) 3% ABPA(4)
% Gel	52%	61%
Density	.13 gm/cc	.13 gm/cc
Cell Size	3-4 mil	2-3 mil
Flexural Mod. - psi	6800 ± 900	6500 ± 1100
Compression at		
5% defl.	108	101
10% defl.	122	116
25% defl.	120	122
Tensile Modulus	6850 ± 1100	5700 ± 900
Tensile Strength	250	260
Elong. at Failure	178	180

- (1) .96 density linear PE, standard Phillips process 5 melt index.
 (2) .95 density PE/butene copolymer, Phillips Cat. 5-7 branches/1000C
 atms. 5 melt index.
 (3) Lupersol-130 - 2,5 dimethyl, 2,5 di(tertiary butyl peroxy) hexyne.
 (4) ABPA - azobisformamide - National Polychemicals, Wilmington, Mass.

TABLE IV

EFFECT OF MELT INDEX ON THE PROPERTIES OF EXPANDED LINEAR PE

Polymer	.960 - .2 MI	.960 - .7 MI	.960 - 2.5 MI	.960 - 5.0 MI
Gel	45	50 - 55	56	51
Density	.14	.13	.135	.14
Avg. Cell Size	2	2	4	2.2
Flexural Modulus	7200	7700	9100	10,700
C-D-5	57	100	32	120
10	85	110	100	130
25	93	110	120	140
Tensile Modulus	6600	7000	-	7900
Tensile Strength	320	370	-	320
Elong. @ Failure	100	300	-	320

TABLE V

MECHANICAL PROPERTIES OF GRAFTED CROSSLINKED POLYETHYLENE-ETHYLENE/VINYLAETATE FOAMED BLENDS

Sample Description	LDPE ⁽¹⁾	85/15 LDPE ⁽¹⁾ EVAc ⁽²⁾	85/15 LDPE ⁽¹⁾ EVAc ⁽²⁾	75/25 LDPE ⁽¹⁾ EVAc ⁽²⁾
Wt. % ABFA	3	3	3	6
Wt. % L-130	.4	0.6	.5	.3
Wt. % Gel	74	75	68	50
Density (gm/cc)	0.134	0.13	0.12	0.06
Cell Size (mil)	6	4.7	5.6	-
Flex. Modulus (psi)	830	640	575	515
Compressive Force (psi) at 5%	24	19	13	1.0
10%	37	30	21	1.5
25%	46	39	26	2.2
Tensile Modulus (psi)	700	640	600	490
Tensile Strength (psi)	200	180	150	80
% Elong. @ Failure	160	140	240	200

(1) 920 polyethylene 1.8 M.L.

(2) EVAc
Copolymer (70 pts PE/30 pts Vac).

TABLE VI

MECHANICAL PROPERTIES OF PE FOAMED BLENDS

Sample Formulation (Ratio HDPE ⁽¹⁾ LDPE ⁽²⁾)	100 0	90 10	75 25	50 50	25 75	10 90	0 100
% ABFA	3	→					
% L-130	.25	0.4	→				
% Gel	51	51	68.6	67	69.4	72.4	74
Density (g/cc)	0.13	0.158	0.154	0.127	0.119	0.123	0.134
Flex. Mod. (psi)	8760	8270	6198	3144	1804	1409	830
Compressive Load (psi) at							
5% defl.	101	132	100	62	38	30	24
10% defl.	111	145	120	79	51	41	37
25% defl.	112	155	123	84	56	46	43
Tensile Modulus (psi)	8700	10,000	8186	4122	2480	1789	698
Tensile Strength (psi)	372	465	395	287	219	183	195
% Elong. @ Failure	305	333	277	232	196	183	162

(1) .960 - .7 MI linear polyethylene.

(2) .915D - 1.8 MI branched polyethylene.

TABLE VII
MECHANICAL PROPERTIES OF EXPANDED POLYISOBUTYLENE MODIFIED POLYETHYLENE FOAMS

Sample Formulation	PF/Polyisobutylene 70/30				
	1%	2%	3%	4%	6%
% ABFA	1%	2%	3%	4%	6%
% L-130	0.4%	0.4%	0.4%	0.4%	0.4%
% Gel	51	54	50	56	58
Density (g/cc)	.4	.3	.18	.135	.07
Flex. Mod. (psi)	16,463	6,932	3,567	3,011	1,316
Compressive Load					
at 5% defl.	298	90	55	33	8.75
10% defl.	406	127	72	46	13.9
25% defl.	526	142	78	49	18.5
Tensile Mod. (psi)	19,400	4700	5,750	2988	1866
Tensile St. (psi)	725	474	422	284	196
% Elong. @ Failure	236	233	219	132	147

POLYETHYLENE FOAM I. MECHANICAL PROPERTIES OF POLYETHYLENE
FOAMS PREPARED AT HIGH AND LOW RATES OF EXPANSION.

by

Dr. C. J. Benning

INTRODUCTION

Our main objective is to produce polyethylene foams economically, with balanced properties of cost/performance. Preparation of expanded polyethylene with optimum properties requires special techniques. Several authors have discussed various techniques at length. Hansen and co-workers have described extrusion foaming, nucleation and specialized "hot spot" techniques to produce fine celled foams. Most of this work was devoted to foams having a density range of 0.3 gm/cc to 0.7 gm/cc.⁽¹⁾ Lasman described the production of foams by compression molding.⁽²⁾ His work emphasized the lower density branched polyethylene foams (.06-0.1 gm/cc). Rubens and co-workers⁽¹¹⁾ were issued a patent that describes an extrusion process for producing low density (.04 gm/cc) PE foams, and later⁽³⁾ discussed the variables that influence the mechanical properties of these materials.

The two properties of major importance in our discussion are resistance to creep and compression-deflection behavior. The most important is creep resistance. Resistance to creep can be obtained by immobilizing the polymer chains, (resins below their T_g and/or having high modulus or high crystallinity at the use temperature). Another approach (which we describe here) is to immobilize the molecules by crosslinking. This can be accomplished by either chemical or radiation techniques. The chemical route has been preferred since chemical crosslinking produces a more homogeneous cure and does not have the problem of size and penetration of radiation.

Our main objective, therefore, is to produce cured low density polyolefin foams with balanced properties and low creep. We investigated 3 procedures to produce low density, low creep foams. These included, techniques for expansion at high and low rates (2000% in <2 seconds to 2000% in

approximately 15 to 20 minutes). The procedures are described below:

EXPERIMENTAL

Procedure I - Atmospheric Expansion of Uncross-linked Plaques at 175°C under N₂

Formulations (Table 1) were prepared by dry blending the ingredients (finely divided resin, liquid peroxide, zinc stearate and blowing agent) in conventional twin shell blenders. Microscopic examination of the blends showed that the polymer particles were coated uniformly with the peroxide, zinc stearate, blowing agent mixture during blending. The dry blend was molded into plaques at 140°C and 2000 psi and oven foamed at 175°C at atmospheric pressure. A comparison of samples prepared in their original molds and those foamed separately in air showed large discrepancies. The plaques foamed between mylar sheets in the molds were white, strong, had high degree of crosslinking (57-66% gel) and were low density. Plaques of the same formulation foamed in air without the O₂ shield of mylar had very large cells; showed signs of decomposition, partial collapse and were not crosslinked. Close control of expansion and crosslinking rates could be maintained when oxygen was eliminated. The density of the degraded foam was (75%) higher, therefore, crosslinked polyethylene foams were prepared in an inert atmosphere to reduce oxidation and maintain crosslinking efficiency.

Rate and degree of crosslinking were varied to determine how foam properties and cell morphology were influenced by the different reactions. Expansion took place in 25 minutes. Specific formulations under investigation are listed in Table 1. The general formula consisted of .95D ethylene-butene copolymer 4.1 melt index (prepulverized) pure peroxide: Zinc stearate, (C.P.) and ABFA. The effects of formulation changes under constant foaming conditions will be discussed later.

Procedure II - Atmospheric Expansion of Crosslinked Plaques at 175°C under N₂

Untreated, unstabilized polymers containing blowing agent and dicumyl peroxide were compression molded into 6"x6" sheets 20 to 40 mil thick on a PHI press at 140°C for 10 minutes (Table 1). Plaques were crosslinked during compression molding to a gel level of 60±2% and expanded in a N₂ atmosphere at 175°C. Expansion was usually complete after 10 minutes. Foams were tested and analyzed to determine the effect of pre-curing on the expansion process, foam structure and mechanical properties.

Procedure III - Preparation of Low Density Chemically Crosslinked PE Foam by Compression Molding

Mixtures of resins, peroxide and blowing agent were compounded in a Banbury between 240-340°F for 1 to 2 minutes. The molten mixture was transferred to a preheated mold and cured under pressure (>300 psi) at 350 to 400°F. The curing agent (2,5 dimethyl-2,5 di(tert butyl peroxy) hexyne - Lupersol 130) and blowing agent (azobisformamide - Kempore 150 - ABFA) decomposed under high pressure to produce a super saturated solution of gas (N₂ - CO₂ and CO from azobisformamide) in the cured resin. When optimum cure (60% insoluble in toluene) was obtained, the pressure was released and the resin expanded uniformly. Expansion took place in less than two seconds.

"Percent Gel" Determination

Approximately 0.3 gram of sample was weighed on an analytical balance and transferred to a 100 mesh stainless steel "basket". The cage was placed in a flask containing 50 ml. of xylene containing 3.0% stabilizer and soaked at room temperature for several hours. The cage was then extracted with refluxing xylene for 24 hours, air dried and then further dried in a vacuum to remove any residual solvent. The "percent gel" is the weight of undissolved polymer.

i.e. W_2 - weight of original foam
 W_1 - weight of insoluble fraction

$$\frac{W_1}{W_2} \times 100 = \text{Percent Gel}$$

RESULTS AND DISCUSSION

Procedure I

Molded plaques containing PE, peroxide, ABFA and activators (Table 1) were expanded under a nitrogen atmosphere to minimize degradation. The foaming cycle was variable at 175°C.

Composites were expanded by two approaches:

First - Formulations containing a low concentration of peroxide (.25 weight %) were expanded. The objective was to determine how expansion prior to curing influenced foam structure and properties.

Figure 1 describes the expansion of high density polyethylene (.95D ethylene-butene copolymer, melt index 4.1) prior to curing. The density decreased in the expected manner with time as the azobisformamide decomposed (gas yield = 230 cc/gm STP).

The expansion process occurred as follows: Isolated cells formed and grew in population size and shape. Although one would expect the cells to deform at the density of closest packing, this was not observed. Deformation of cell walls started at a density of .35 gm/cc. Cell structure A and B in Figure 1, graphically illustrate the cell structure. Many tiny cells (<25 micron) populated the strut area in the boundary region between large cells. As the cells walls become more distorted and compressed, the cells began to rupture and coalesce. At structure C (Figure 1), the foam did not support itself under the stress of continued expansion and partially collapsed. The density rose. The foams did not completely collapse, however, because the melt viscosity had increased as the peroxide decomposed and stabilized the foam. Large cells, heavy cell walls and struts were formed from the coalesced smaller cells.

The final structure consisted of irregular cells, approximately 550 to 1500 microns in length and width.

Photographs A, B, and C illustrate these structures. The compression deflection behavior of foams having cell structure A, B, and C are illustrated in Figure 2.

Curve A (Figure 2) describes the stress-strain of foam A under compression. Foam A was a high density foam (.64 gm/cc). Curve B records the C-D curve of the lower density (0.2 gm/cc) foam with slightly larger cells. The compressive strength of Foam C is the result of low density (0.1 gm/cc) and the non-uniform structure chemically crosslinked during the last stages of expansion.

To summarize:

This method (Procedure I) of producing cellular materials (slow expansion followed by curing) produced foams having large cells. During the expansion process the polymer has a low viscosity therefore, cells expand, and coalesce. Some cell walls melt and flow into the strut area (junction between the cells). This produces large cells and heavy crosslinked struts.

The second method of preparing foams in Procedure I was to increase the rate and degree of cure by adjusting the peroxide concentration. Figure 3 shows the effect of peroxide concentration on degree of cure of the composite. The half lives of the peroxide (L-130) and azobisformamide (ABFA) are similar enough (see Figure 4) to allow good interaction. Lasman⁽²⁾ reported that the rate of decomposition of ABFA could be altered by addition of heavy metal salts. Therefore, the rate of cure and the rate of decomposition can be controlled within desired limits.

The effect of crosslinking during expansion is recorded in Figure 5. Cell structure D formed initially, as the sample expanded. Expansion was similar to that observed in structure A (type I foams) discussed in Figure 1. The foams exhibited similar compression-deflection behavior. The composite continued to expand while the melt viscosity of the resin increased rapidly and stabilized the foam. At 15 minutes maximum gel was obtained and the cells continued their expansion. As a result of this continued expansion, elongated cells oriented in the direction of expansion were formed. The cell windows stretched but did not break (structure E).

Cell structure E, (Figure 5) resulted from the stabilization due to crosslinking. The cells were more than 95% closed, and were the result of the higher extensibility of the cured polymer, thus allowing the cells to grow and stretch without rupturing the film in the windows.

One would expect the foam with elongated cells in structure E to have directional properties, and indeed it does. Figure 6 describes the stress-strain behavior of Foam E under compression parallel and perpendicular to the direction of expansion. As one would expect, the large concentration of heavy struts, and elliptical cells caused a sharp rise in compressive strength at low deflection (5%) while traverse compression produced a greater deflection at lower pressure.

We have produced foams having the identical chemical structure as Foam E, in addition to a balanced cell geometry. The procedure was to reproduce the chemical reactions and structures, but allow three dimensional expansion without restraint. The balanced foams were prepared by atmospheric expansion during free fall of an extrudate through a vertical curing zone. Photos x and y show the cell structure of these foams. The density of foam x is 0.1 gm/cc and foam y is .06 gm/cc. The compression deflection of these foams was balanced.

Procedure II

Molded plaques containing resin, dicumyl peroxide and blowing agent were cured to a gel level of 60% \pm 2% without destroying the blowing agent. Cured samples were expanded in an oven under standard conditions (175°C).

Figure 7 describes the slow expansion of cured composites. As we observed in Procedure I, Figure 1, the initial cell structure was a series of minute cells that grew in population and size as expansion proceeded. The final structure was an infinite series of cells having integral walls and contained less than 5% open cells. Expansion of these cured mixtures produced more uniform foams with smaller cells than Procedure I. The compression deflection curves are more uniform and are illustrated in Figure 8 and 9. These type II foams have 200% higher tensile strength, improved compression behavior. The cell size is 125 to 500 microns compared to 550 - 1500 microns for type I foams.

Figure 8 describes the compression deflection behavior with increasing density. The cell structure was essentially constant (>90% closed cells). We

noted a variation in cell size with degree of cure, for example, cell size decreased with increase in cure and was directly dependent on particle size of the blowing agent⁽²⁾ heat transfer and uniformity of dispersion.

The effect of large cells vs. small cells is illustrated in Figure 9 which compares the compression deflection of foam E and G.

Procedure III

This procedure has been used by several authors to evaluate blowing agents. Papers and patents have also been written that describe the versatility of the process for evaluating resins and blends of resins^(2,4) and for preparing foams with tailored properties. The recipes described in this section are recorded in Table 1.

Unlike Procedure I and II, Procedure III was carried out at very fast expansion rates i.e. a 1 gm/cc composite expands to 0.05 gm/cc in <2 seconds (2000% increase in volume in <2 seconds).

These rates of expansion approach impact velocities and the stability of foams prepared by this Procedure (III) is very dependent upon elasticity and therefore, the viscoelastic behavior of the resin system at high temperatures and high rates of extension. The stability of foams therefore, will depend on degree of cure, molecular weight of resin, structure of resin, etc. We have noticed that as the expansion rate is increased, additional emphasis must be placed on the rheological parameters. For example, a high activation energy of flow is desired in a resin at high rates of stress and strain to stabilize the foam. At low stress-strain rates, (type I and II foams) one can expand conventional resins in the same manner as one would expand a sponge or blow a film. In fact, excellent foams can be prepared at 0.1 gm/cc (6 pcf) without reinforcing the resin or modifying its viscoelastic properties by cross-linking as long as the temperature is controlled and the rates of expansion are maintained at a low level.

Figure 10 describes the expansion characteristics of four linear polyethylene resins of different molecular weight (60-002E = .96D - 00.2 melt index ethylene polymer). Approximately, .2 to .3 wt. % L-130 (2,5 dimethyl - 2,5-(di-tert butyl peroxy) hexyne) is required for stability of compression molded low density linear

polyethylene foam. For the higher molecular weight resins (0.2 melt index) less peroxide is required. A minimum of 20 to 30% gel is required for these linear PE's for foam stability. LDPE resins have similar requirements, however, LDPE (0.915D - 1.6 melt index) can be stabilized at a lower gel level, i.e., 10 to 20 wt. % (See Figure 11).

Analysis of the cell structure of type III foams showed the following:

1. Foams contain >95% closed cell. Cell size (average) is between <1 to 7 mil (<25 micron to 175 microns). The cell walls appear to be wrinkled as if they are under vacuum.
2. The cells decrease in size as degree of cure increases, and density increases.
3. Smallest cells produce the strongest foams, these cells have optimum size (<75 micron) at 60% gel and at 0.05 gm/cc (4 pcf) for linear PE and 30% gel for LDPE at .05 gm/cc.
4. Linear PE foams are less stable at low cure (20-30%) and low density (.03 to .05 gm/cc) than branched PE.

Type III foams have the most uniform structure, lowest creep and highest tensile strengths.

Type I and type II foams were prepared at slow rates of expansion (3-25 minutes) and type III foams at the fast rate (<2 seconds). Procedure I was designed to study the effect of relative crosslinking and expansion rates on cell morphology and mechanical properties. Procedure II, was used to determine the effect of prior curing and Procedure III crosslinking before expansion under pressure.

Type I foams (prepared by Procedure I) were expanded in an open mold. Type II and III (prepared by Procedure II and III) were expanded in three directions with balanced properties.

It has been stated that cell size, polymer modulus, and cell structure determine the initial stress-strain of the foam under compression, while the tensile and flexural properties are mainly dependent upon foam density and polymer modulus.

Figure 12 illustrates the effect of molecular weight and modulus (as molecular weight increases, modulus decreases and foams are somewhat softer) on compression deflection.

As the base resins become less crystalline or more flexible the foams are softer. (Figure 13).

The description of Procedure I, II and III is now complete. We have evaluated these three general types of foam and have compared their properties.

Compression-deflection, modulus (flexural and tensile) and strength are of major importance. These properties are determined by cell morphology and polymer properties.

Cell Morphology

It was reported that the compressive strength at 25% deflection increases with increasing cell diameter for latex foam rubber of different densities.⁽⁵⁾ Previous investigators⁽⁶⁾ of high density foam rubbers obtained opposite results. We have analyzed the compression of foams as a distortion or bending of the heavy sections between the cells. The dependence of compressive strength upon cell size and shape has been shown in Figure 2, 6 and 9. Figure 6 illustrated how non-uniform (directional) cells can drastically alter C-D values. Figure 9 describes the effect of cell size on compressive strength.

Initial compressive moduli of these three foam types are quite different. A prominent plateau exists in the curve for large celled foams, and those having cells preferentially, oriented in one direction (Figure 6). These differences in structure and properties compare favorably with the mechanical model presented in earlier articles.⁽³⁾ Figure 14 compares the model structure (presented in Ruben's paper⁽³⁾) with predicted stress-strain behavior under compression. This is in excellent agreement with the compression deflection of foam E described in Figure 6 and 9.

We have further examined foam E during the compression process with a stereomicroscope to determine the reason for the plateau in the C-D curve.

The mechanism of compression is as follows: As a type I foam (composed of large cells - 500 to 1500 microns) is compressed, the outside layers of cells absorb the initial stress of compression. At 5% to 10% compression, most of the struts do not distort. Above 10% compression struts are buckled, and at 25% compression, the outer layers of cells are telescoped into their neighbors. At 25% compression the inner cells only change dimensions 10% while cells at the center of the specimen are only 3-5% distorted.

Type III foams composed of small uniform cells (25 to 150 microns) exhibited a different behavior under compression. At low compression (5% - 10%) all the cells appeared to absorb the force uniformly and were compressed about an equivalent amount. Distortion was slightly reduced in the cells more distant from the point of stress, however, there was no drastic bending or collapsing of the struts described previously, but rather a uniform squeezing of cells.

The foams resemble an infinite series of polyhedron with spherical segments. The cells located closest to the point of stress become elliptical. Distortion continued to above 25% compression. The absence of a plateau in the compressive stress-strain curve of type III foams, therefore, is caused by the capability of small celled foams to transmit and distribute the energy or stress of compression. One would perhaps, expect significant contribution from the compressive resistance of the gas and the modulus of the resin. The tear strength or impact strength of the cell window will also contribute to this strength, however, this depends on speed of compression.

Sandridge, et al⁽⁷⁾, reported that compressive and tensile properties rise as the amount of closed cells increase, until unstable foams are produced. We have found that as the foam structure becomes more uniform and closely packed the foams become stronger. It is also reported^(3,5) that foams produced initially, as closed-cell foams, and subsequently, crushed to produce an open-celled foam, have lower strength than do foams which were produced originally as open-celled foams. The conclusion was that the

polymer in the broken cell walls of the crushed foam does not contribute significantly to the properties, and the original open-celled foams are prepared in such a manner that the cell walls have retracted back into the rib structure and can contribute to the physical properties.

We have visually examined foams during crushing and we find that if one crushes a foam as little as 25 to 50% several mechanisms are involved, depending on cell size and foam density. For example;

- (1). For large celled foams (>500 micron) the cells are packed in a "staggered" fashion. Upon compression, one cell layer will be forced into the second layer. This telescoping rips cell walls and struts. Loss of tensile is due to partial destruction of cell walls, struts and tear initiation.
- (2). The more elastic foams transmitted, the more energy through the structure without loss in properties.
- (3). Foams made up of small cells exhibit a loss in tensile when compressed beyond 25%, because the cells walls are ruptured and tears are initiated that propagate into the thin thread-like struts when tensile tested. (Similar to a notched tensile strength). (One must always remember that a tensile test is the test of the weakest component).

Polymer Properties and Foam Properties

Density

The effect of foam density (volume fraction of polymer present) on the physical properties of flexible foams has also been investigated.^(5,9) The increase in tensile strength and flexural modulus with increasing density has been noted and quantitative relationships have been presented (Gent and Thomas)⁽⁹⁾, for tensile and compressive behavior of foamed elastic materials with respect to the modulus and volume fraction of the plastic phase. A large number of miniature rods represented the struts in their model for foamed structures.

To our knowledge, there is no data available on the variation of these moduli for low density or linear polyethylene foams.⁽³⁾ These theories serve to help us understand the behavior of foams and the data we have accumulated should guide us in making predictions of properties of proposed foams.

Figure 15 and 16 illustrate how tensile properties of Type III compression molded foams are effected by the volume fraction of the resin. The data points in Figure 15 represent foam measurements and can be extrapolated to the parent unoriented crosslinked resin.

Figure 16 illustrates how the tensile properties of a Type III foam prepared from a mixture of two polymers (PE - PIB) grafted and crosslinked together are effected in an identical manner.

The flexural modulus of a Type III foam is also the result of the modulus of the polymer in the foam and its volume fraction. Figure 17 describes the flexural modulus of foams prepared from resins having a wide variation of flexural modulus. For example, co-crosslinked low density polyethylene foams have very low modulus when compared to linear polyethylene.

Creep of Uncrosslinked PE and Expanded PE

The dimensional stability of polymers and cellular products is essential in many applications.⁽¹²⁾ A rigid, solid plastic or a rigid cellular plastic should be able to withstand modest compressive loads without deformation for long periods of time. A flexible foam must be able to withstand compression without a permanent deformation or change in shape; i.e. mattresses, cushions, etc. These illustrate the importance of creep behavior.

Creep tests can be carried out in compression or tension. A constant load is applied to the sample and deformation is measured as a function of time in the tensile creep test. A more meaningful test of foams is creep recovery. Recovery is the time dependent portion of the decrease in strain following unloading the sample.

The creep behavior of a branched polyethylene at room temperature is shown in Figure 18. The greater the load the greater is the creep elongation and creep rate. These curves are representative of plastic or viscoelastic materials. The samples have an instantaneous

elongation immediately after the load is applied. Deformation is inversely proportional to molecular weight, and elastic modulus. The period after the initial deformation is followed by a period in which the rate of creep gradually decreases to a constant rate. In the extreme case, it approaches zero, this means that the deformation may reach a nearly constant value at long times. Recovery is an essential property in the creep behavior of flexible and semi-rigid foams and can be expected to depend on density and the polymer structure.

In most creep tests there is a measurable recovery when the load is removed, therefore, creep must consist of a viscosic component and an elastic component.

The elastic component comes from chain entanglements, therefore, as the molecular weight (degree of entanglement) increases creep recovery should increase. This should also be time dependent for uncrosslinked polymers. For example, creep recovery is usually greater in short creep tests than in long ones. This is also observed in expanded uncrosslinked polymers (Figure 19). If the number of entanglements decreases with time one should observe a decrease in creep recovery with repeated compression tests. Figure 20 shows the creep recovery of a commercial uncrosslinked PE foam (2 pcf - solvent expanded) at two different temperatures.

The amount of entanglement should be less at the higher temperature, therefore, less recovery. Creep recovery is lower, as predicted, in the second test (RT_2), because of a decrease of entanglement.

The crystallites in crystalline polymers like PE act like crosslinks in modifying the creep behavior of polymers above their glass transition temperature. A polymer chain may tranverse several crystalline and amorphous regions and thus acts as a psuedo crosslink.

The modulus (and creep resistance) of crystalline polymers and their expanded composites is quite temperature dependent compared to crosslinked rubbers or rigid amorphous polymers at temperatures well below the T_g . One would expect to see this in the

creep recovery of expanded crystalline polymers. Figure 20 shows the drastic decrease in creep recovery of a PE foam at 23°C and 35°C. The crystallinity of the resin is of the order of 55 to 60% as measured by X-ray. Neilson⁽¹²⁾ states that several factors may contribute to this high temperature sensitivity of creep properties. First - the degree of crystallinity changes with temperature, Second - recrystallization may occur and third, rate of crystallization depends on temperature. The creep properties of crystalline polymers may also be due to rotation and motion along the slip planes of crystallites and crystallite breakage. These factors may tend to make the creep greater than one would normally expect from a crystalline polymer with rigid and permanent crystallites.

The creep behavior of a typical crystalline polymer (PE) is compared with an amorphous polymer (polystyrene) in Figure 21⁽¹²⁾ at 25°C. This temperature is below the T_g of polystyrene so it creeps only slightly. Polyethylene is above its T_g and although it is highly crystalline it has a large elongation and a high rate of creep.

Creep of Crosslinked PE and PE Foam

Below T_g little chain motion can occur, therefore, crosslinking has little effect on creep properties, unless the molecular weight between crosslinks is small, for example, one or two monomer units. In this special case, the materials have very high T_g's. Often polymers of this structure decompose before they soften, therefore, they exhibit practically no creep.

One would expect the major advantage of crosslinking PE to be at a point where crystallinity disappears, i.e., above the crystalline melting point. The Table below illustrates this point.⁽¹³⁾

	<u>LDPE (a)</u>	<u>LDPE</u>	<u>HDPE</u>	<u>HDPE</u>
Melt Index	2.0	0	4.1	0
Tensile Strength -23°C	1800	2280	2700	4600
% Elong. @ Fail.	600	500	170	280
Tensile Strength - 160°C	Flows	100	Flows	80
% Gel	0	88.3	0	98.0

(a) 0.919D PE.

(c) .96D PE 4.1 M.I. (Phillips Process Linear PE)

Usually crosslinks have a dramatic effect on creep above Tg. Linking chains together with chemical bonds changes the viscoelastic material to a highly elastic material. Ideal crosslinked polymers should; (a) stretch a given amount when a load is applied, (b) the amount of elongation should not change with time and (c) when the load is removed, the sample should recover its original length. Figure 22 and 23 illustrate the creep behavior of .95 and .96D ethylene polymers. When the load is applied there is an instantaneous deformation. The rate of change of elongation with time decreases with increasing degree of cure (gel). When the load is removed the highly crosslinked materials (96% gel) approach their original dimensions. Usually a small amount of crosslinking is needed to greatly reduce the creep, however, a high degree is required to approach the ideal rubber.⁽¹²⁾ The reason is that the crosslink network is imperfect and there is always a small amount of soluble component.

Although our investigations are not complete, it is evident that crosslinked, uniform foams of low density have the best creep recovery properties; i.e., Type III > I. One would expect the improvement in creep to be more pronounced at high temperatures, and to depend on the degree of cure.

Crosslinked PE foams are slightly more resistant to creep than uncrosslinked PE. This is illustrated in Figure 24 by the higher creep recovery. The effect of different degrees of cure on creep recovery is shown in Figure 25. As we would predict the more crosslinked structures have better creep recovery.

A more complete evaluation of the creep properties of Type III foams will come later.

SUMMARY AND CONCLUSIONS

We have described three types of polyethylene foams. The foams prepared from cured systems, Type II and III are superior to those cured during expansion (Type I). Type II and III foams have smaller cells and are stronger composites.

Cell structure determines the performance of a low density foam. Type II and III foams are superior because they have balanced structure and properties.

Low creep is also a major attribute of Type III foams because one would expect creep to depend not only on degree of cure but also on structural integrity.

Pressure expansion (Type III) appears superior to atmospheric expansion (Type II) because the increase in cell size with decreasing gel and density is more pronounced in II than in III. Type I foams are prepared by a process that caused non-uniform cell size; because of diffusion and coalescence and is undesirable because the compressive strength is deteriorated.

Three processes have been reviewed and the product performance analyzed.

ACKNOWLEDGMENTS

The author wishes to express his thanks to the W. R. Grace Research Division for their permission to publish this research. Thanks are also due to Mr. R. L. Adams who prepared the foams and helped develop the various processes, and Mr. G. Fulmer who supervised the tensile testing of the foam samples.

BIBLIOGRAPHY

1. Hansen, R. H., "Production Of Fine Cells In The Extrusion Of Foams", S.P.E. Journal 1877-82 (1962).
2. Lasman, H. R., "Foaming Agents For Polyolefins", S.P.E. Journal 18, 1184-91 (1962).
3. Skochdopole, R. E. and Rubens, L. C., "Physical Property Modifications of L.D.P.E.", Modern Plastics, 1965.
4. Benning, C. J., "Physical Properties Of PE Foam - A New Approach To Preparation Of Grafted-Crosslinked Systems", Wayne State University, "Polymer Conference Series, Cellular Plastics", May 9-14, 1966.
5. Talaley, J. A., I and E.C. 46, 7,1530 (1954).
6. Church, H. F., Trans. of Inst. Rubber Ind. 4, 533 (1928).
7. Sandridge, R. L., Gemeinhardt, P., and Saunders, R. H., ACS Meeting, Chicago, Ill., (1961).

8. Saunders, J. H., and Frisch, K. C., "Polyurethane Chemistry and Technology", Part I, Chemistry Interscience Publishers, New York, 1963.
9. Gent, A. N. and Thomas, A. G., 7th. Annual Technical Conference Proceedings, Cellular Plastics Division, Soc. Plastics, Ind., New York City, N. Y., April, 1963.
10. Fulmer, G. E., Benning, C. J., "Mechanical Properties Of Crosslinked Linear Polyethylene", 21st. Annual Technical Conference S.P.E., March, 1965.
11. Rubens, L. C., et al U.S. Patents 3,067,147 - "Process For Foaming And Extruding Polyethylene Using 1,2-Dichlorotetrofluoroethane As The Foaming Agent".
12. Nielson, L. E., "Mechanical Properties Of Polymers", Reinhold Publishing Corp., Library of Congress #63-18939.
13. Donotto, S., "Mechanical Properties Of Crosslinked Ethyl Acrylate Copolymers", 21st. ATEC, Vo. XI, Technical Papers, Boston, Mass., March, 1965.

TABLE I

COMPOSITION AND PROCESS ELEMENTS

<u>Composition</u>	<u>Procedure I</u>	<u>Procedure II</u>	<u>Procedure III</u>
Resin	100(1)	100(1)	100(1), (6)
Blowing Agent	.2-7(3) wt. %	2-7(3) wt. %	2-7(3) wt. %
Organic Peroxide	.25-1(2) wt. %	1 - Dicap(5)	1(2)
Lubricants and Additives	.5 ZnSt. (4)	.5 ZnSt(4)	.5 ZnSt(4)
<u>Process</u>			
Dry Blending	20 min./23°C	20 min./23°C	Banbury - 1-2 min/120-170°C
Comp. Molding	6 min./140°C	10 min./140°C	-
Expansion	25 min./175°C (N ₂ - Oven)	15 min./175°C (N ₂ - Oven)	6 min/195°C/>300 psi
(1) 95D - Eth-But Copolymer 4.1 M.I.			
(2) 2,5 dimethyl-2,5 di(tertbutylperoxy)hexyne.			
(3) Kempore 150 - Azobisformamide (concentration was varied between 2-7 wt. %).			
(4) Zinc Stearate concentration was varied between .5 - 3 phr.			
(5) Dicumyl peroxide.			
(6) LDPE .915D - 1.6 M.I.			

FIG. 1
PROCEDURE I EXPANSION
Rate Expansion > Rate Crosslinking

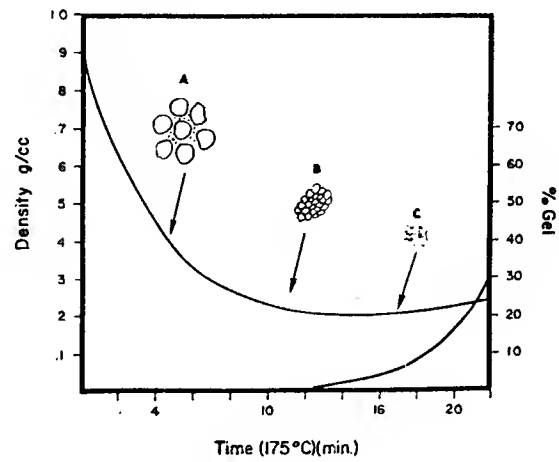


FIG. 2
COMPRESSION DEFLECTION OF EXPANDED
PE BEFORE CURE

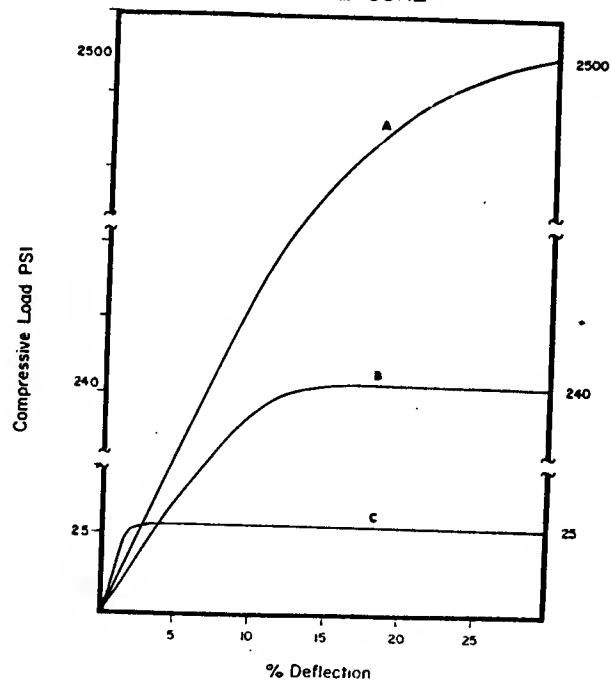


FIG. 3
EFFECT OF PEROXIDE CONC. ON DEGREE
OF CURE

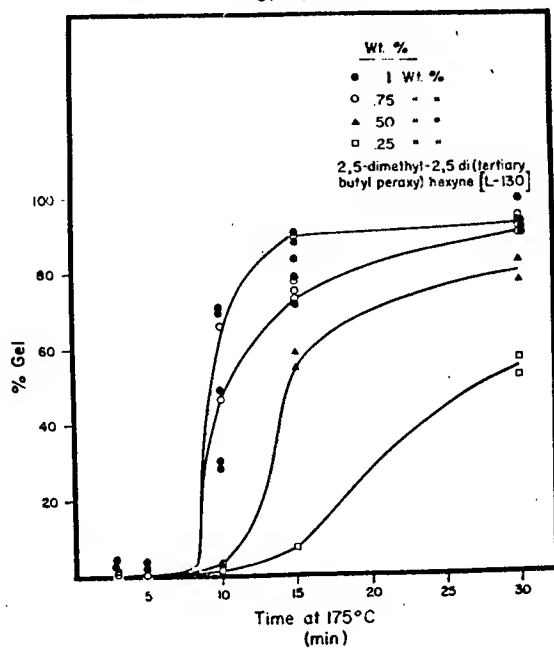


FIG. 4
COMPARISON OF HALF LIVES L-130/ABFA

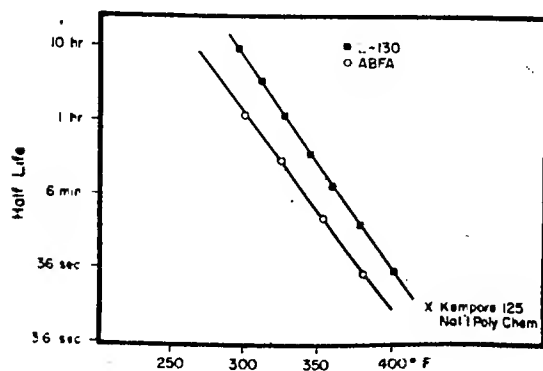


FIG. 5
PROCEDURE I EXPANSION
Rate Expansion = Rate Crosslinking

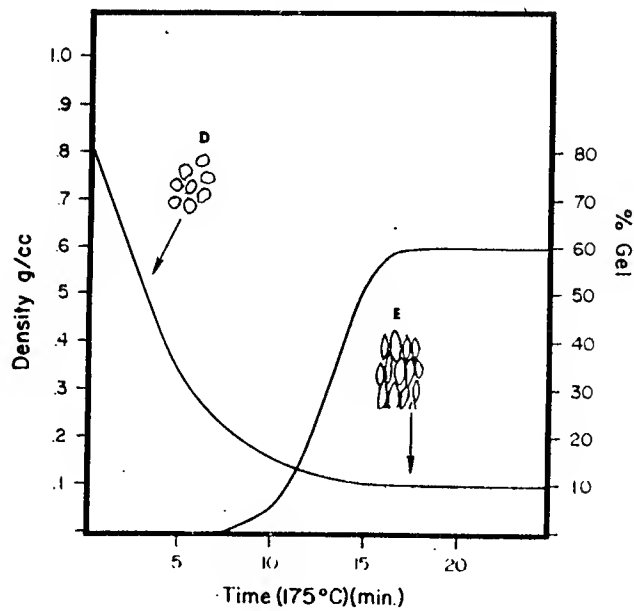


FIG. 6
COMPRESSION DEFLECTION PROPERTIES
OF UNBALANCED FOAM

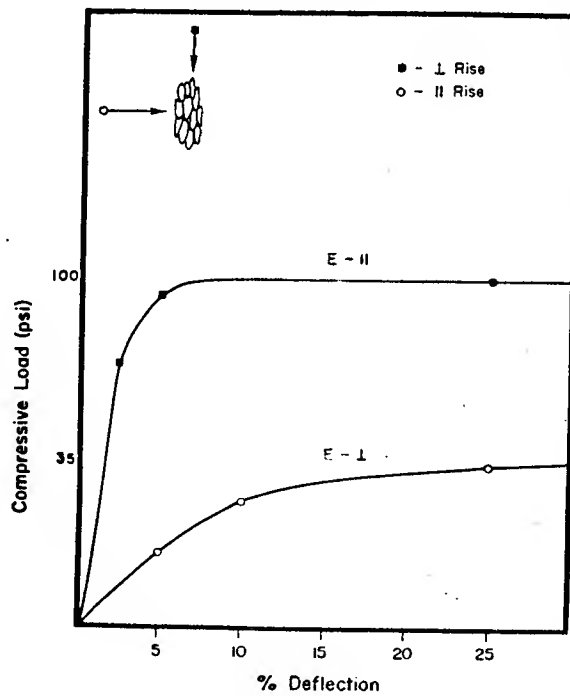


FIG. 7
PROCEDURE II
EXPANSION OF CURED COMPOSITES

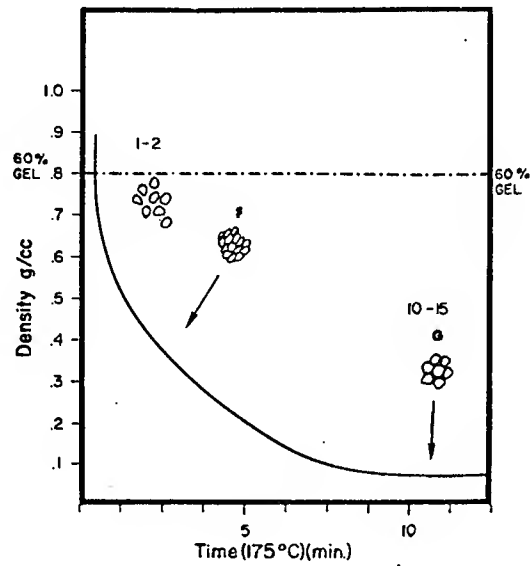


FIG. 8
EFFECT OF DENSITY
ON COMPRESSION DEFLECTION

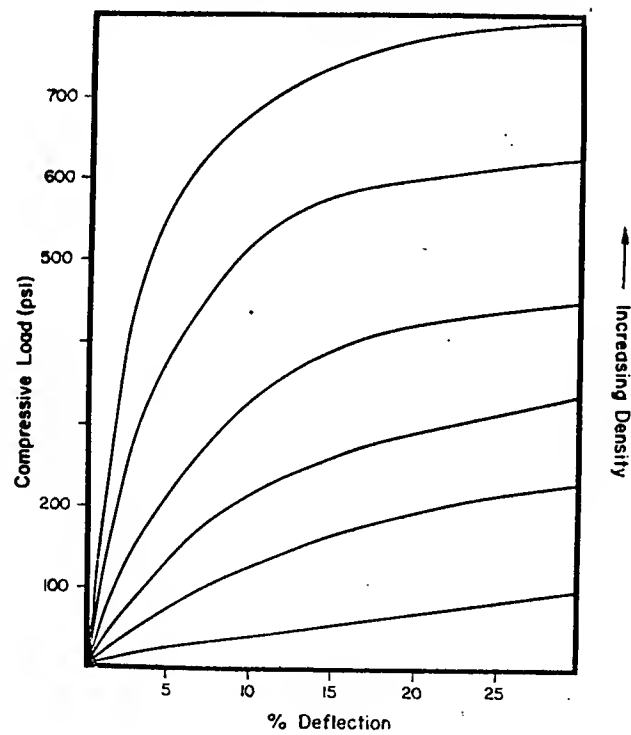


FIG. 10
STABILITY OF LINEAR PE
COMPRESSION MOLDED FOAMS

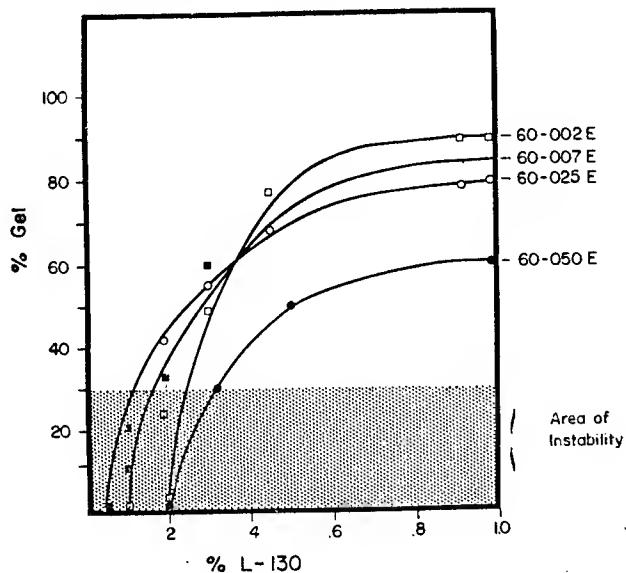


FIG. 9
EFFECT OF CELL SIZE

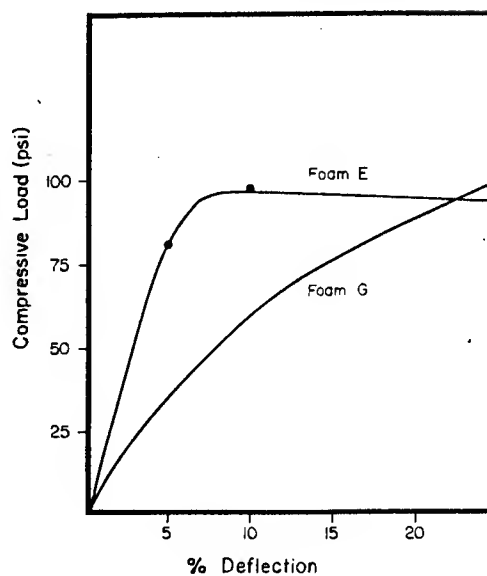


FIG. 12
EFFECT OF MOLECULAR WEIGHT
ON COMPRESSION DEFLECTION

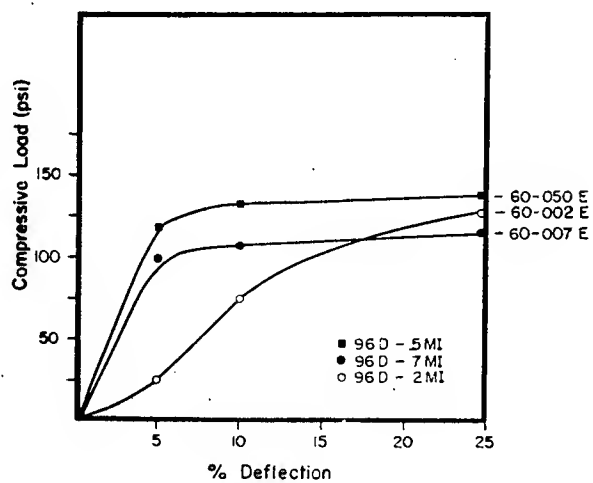


FIG. 11
STABILITY OF COMPRESSION MOLDED
LOW DENSITY PE FOAM

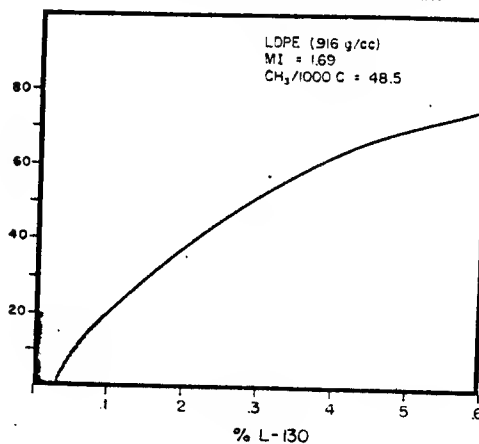


FIG. 14

MECHANICAL MODEL FOR PE FOAM COMPRESSION

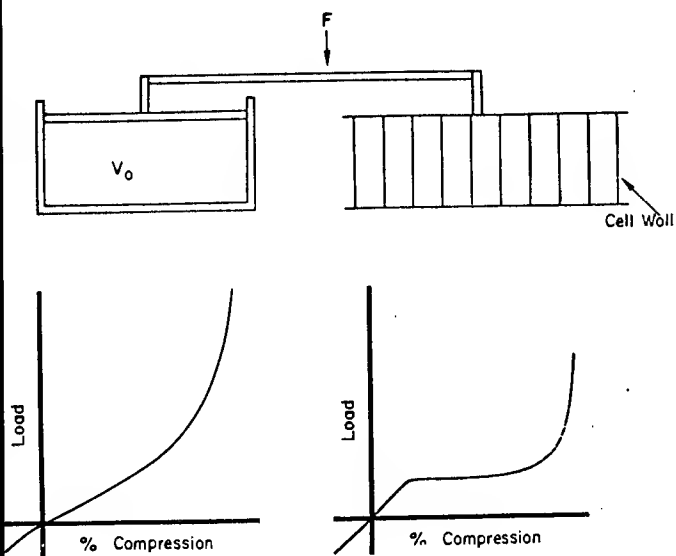


FIG. 13

EFFECT OF MODULUS ON COMPRESSION DEFLECTION

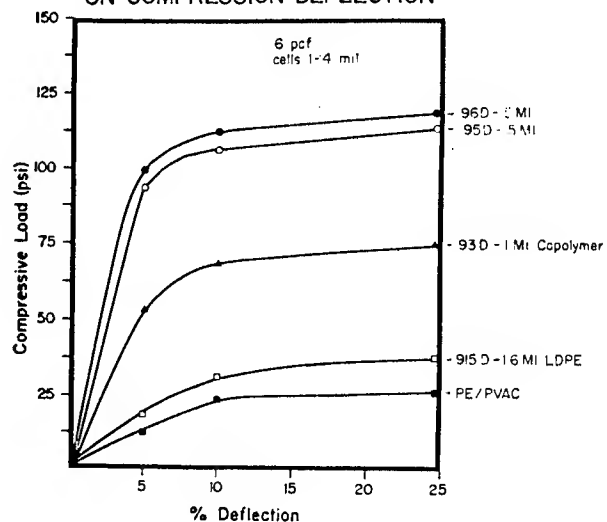


FIG. 16

POLYETHYLENE - POLYISOBUTYLENE FOAMS

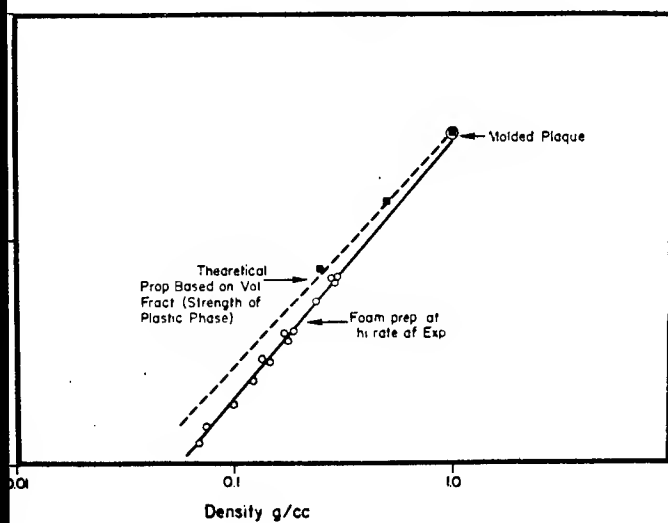


FIG. 15

TENSILE PROPERTIES OF PE FOAM VS. DENSITY

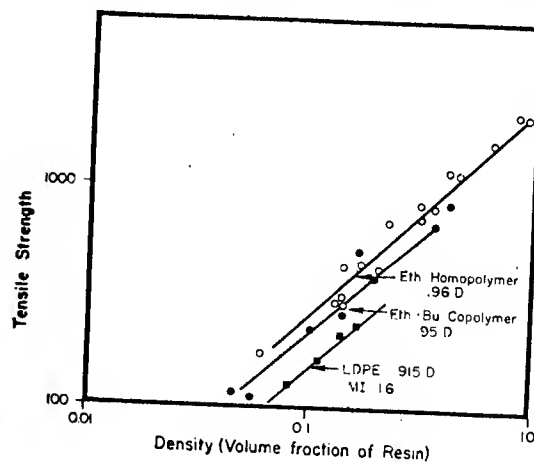


FIG.17 EFFECT OF DENSITY (Vol. Fraction of Polymer) ON FLEXURAL MODULUS

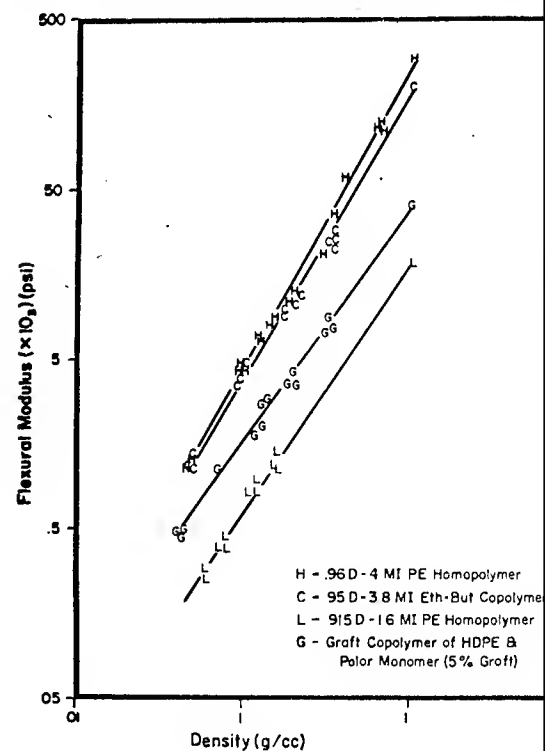


FIG 18
CREEP OF POLYETHYLENE AT
200, 400, 600, & 800 PSI

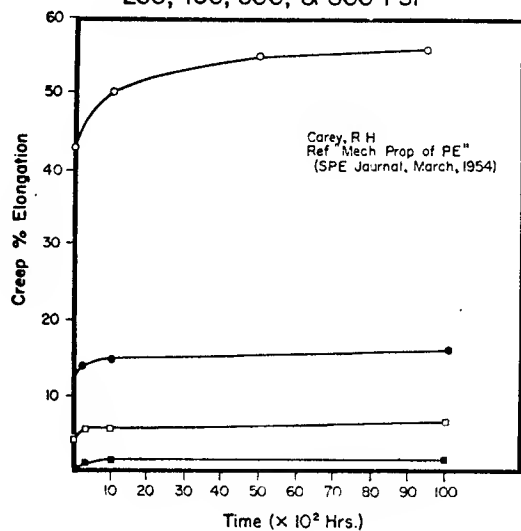


FIG.20 RECOVERY OF SOLVENT EXPANDED LDPE (UNCROSSLINKED)

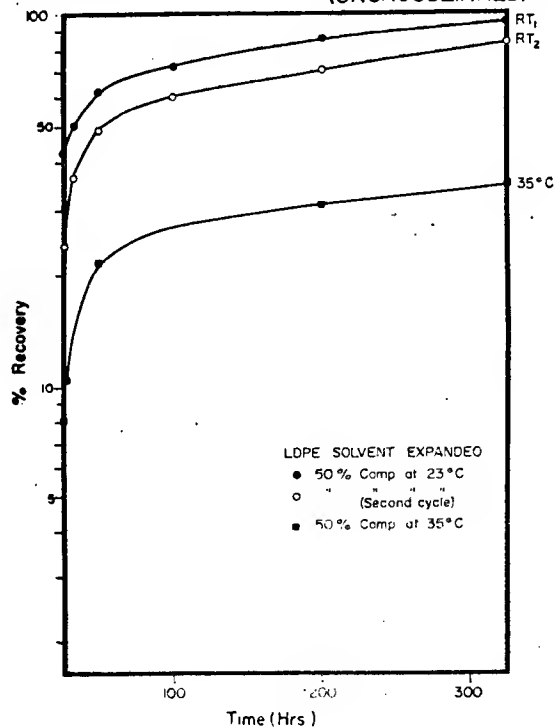


FIG 19
CREEP RECOVERY FOR LDPE FOAM

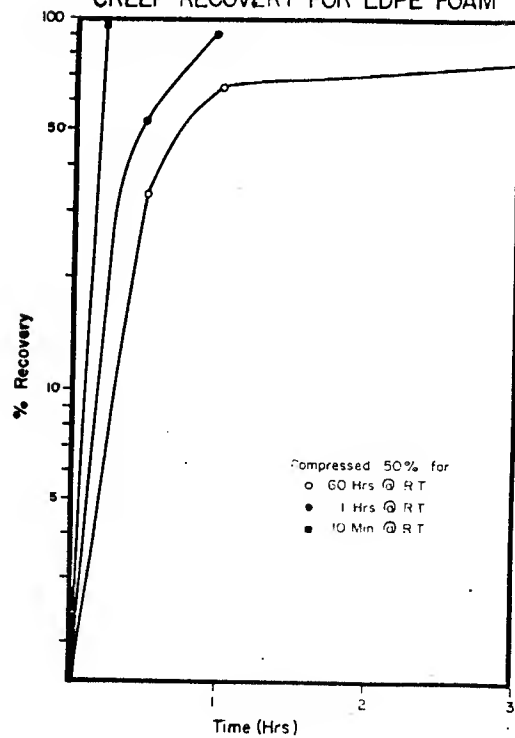


FIG 22
CREEP OF CROSSLINKED HDPE (10 psi 161°C)

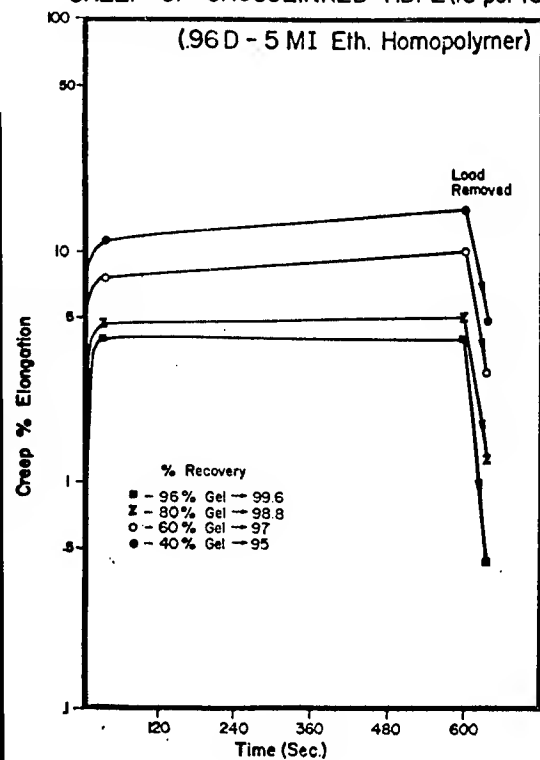


FIG. 21
CREEP OF CRYSTALLINE
& AMORPHOUS POLYMERS

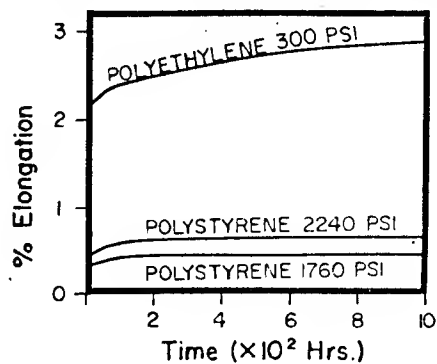


FIG 23
CREEP OF CROSSLINKED HDPE (10 psi 161°C)

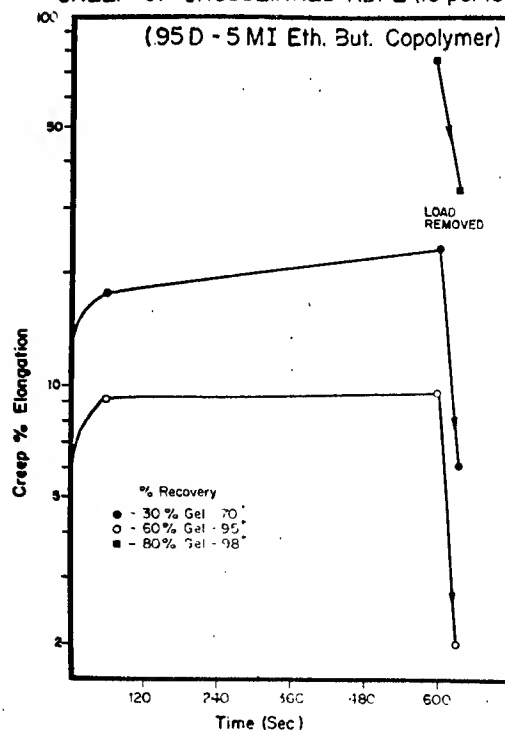


FIG. 24
RECOVERY OF CROSSLINKED & UNCROSSLINKED
PE FOAMS AT 23°C

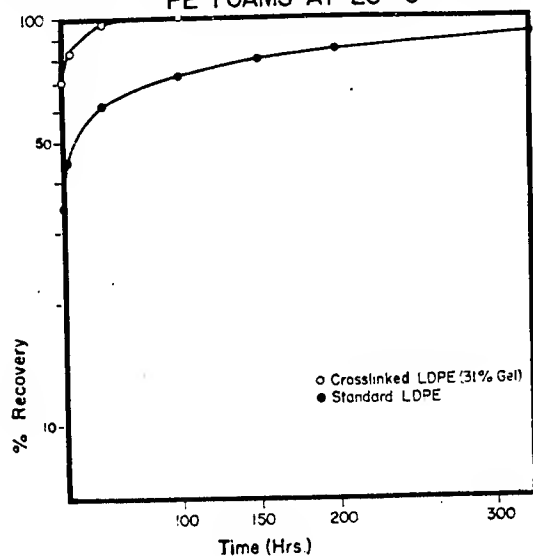
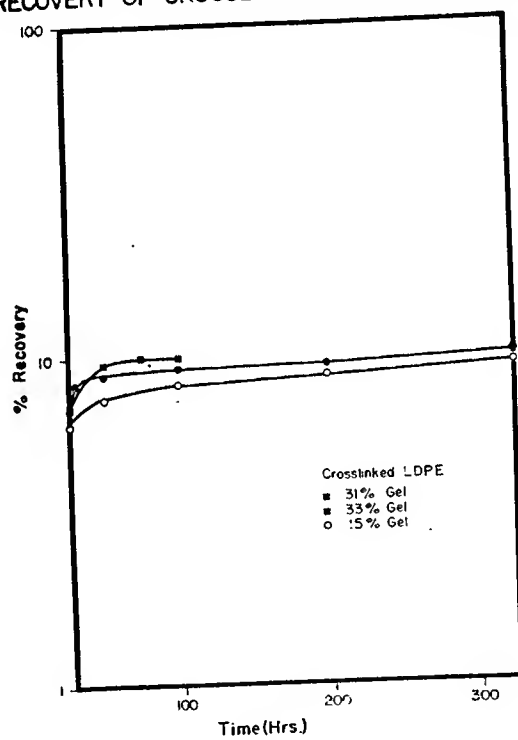


FIG 25
RECOVERY OF CROSSLINKED PE FOAMS AT 23°C



THE FORMATION AND EXAMINATION OF CELLSIN EXPANDABLE POLYSTYRENE FOAMS

By

A. R. Ingram
Research Department, Koppers Co., Inc.
Monroeville, Pa.

*Myrmecophilous
Polymer Research*

Introduction

Most rigid plastic foams today are made from polystyrene. In 1966 the total market for polystyrene foam was reported to be 160 million pounds, while that of rigid polyurethane was 92 million pounds (1).

Polystyrene foams exist in a variety of forms - from 2-foot thick docks at marinas to 5-mil thick films for decorative lamination; from coffee cups to portable refrigerators; and from pharmaceutical packages to carboy containers. The raw material for producing such foams is expandable polystyrene, consisting of plastic particles with volatile hydrocarbons trapped among the rigid polymer chains. The foams may be produced by molding or extrusion methods. The molding method involves two steps: first, the pre-expansion step in a continuous, upward flow of steam and agitated beads; and second, the molding step whereby the aged foamed particles are further expanded by steam, at superatmospheric pressure in a slightly vented mold, to fill the empty spaces and to fuse together. The molding step is completed by circulating or spraying cooling water in the jacket of the mold until the foam no longer exerts pressure. The extrusion method to make film or sheet involves the processing of a mixture of expandable polystyrene granules and a cell-nucleating agent in blown tubular film extrusion equipment. The extrusion method of producing board employs methyl chloride as a blowing agent.

In this presentation we wish to discuss particularly some of our own studies of the microscopy and formation of foam structures from polystyrene (2, 3, 4). The pertinent literature will also be reviewed.

Light Microscopy

Molded or Extruded Boards

With foams of relatively large cell diameters (5 to 10 mils or more), it is possible to cut suitable specimens with a razor blade, microtome or automatic meat slicer. Such samples are thin enough for light to pass without obstruction between most of the cell walls. Figure 1 shows the equipment which was used in cutting some of the foams of this investigation. A 1.25-inch diameter cylinder of foam is cut with a mechanically driven cork borer and the plug of foam is fitted snugly into a cylinder. The foam is positioned manually for cutting by a single-edge razor blade held in a device specifically developed for this purpose. The specimens are then mounted between 2 x 3-inch microscope slides, being careful not to crush the foam.

As the cells become smaller than 5 mils in diameter, it becomes increasingly difficult to cut specimens thin enough to see between the cell walls yet thick enough to avoid rips and ridges. A method illustrated in Fig. 2 was therefore devised to prepare specimens of 2-mil thickness.

A 5/8-inch diameter x one to two-inch long cylinder of foam is cut with a sharp cork borer. The foam is pushed to the "back end" of the borer by a wood plug. The assembled borer, foam and wood plug are positioned as indicated in Fig. 2 in a device by which the wood plug can be advanced by a fine-threaded screw attached to a knob. The knob may be placed over a dial calibrated to read in two mils of advancement of the foam. The foam is then

While the boundaries are discernible, they show very little densification of foam beyond that of slightly compressing one layer of the fused cells. When such a foam is torn, it exhibits a random pattern of rupture - through bead boundaries as well as along them.

This foam specimen is also magnified to X170 to show the cell structure in detail. By such a view one can appreciate the fact that air occupies 98.6% of the volume of a foam of 1.0 lb/ft³ density. The photograph shows cells with both top and bottom sheared away - depicting a strut-and-window pattern with a very high concentration of material in the struts.

In Fig. 4 is shown in X5 magnification a foam with the largest cells about 12 mils in diameter and the smallest about 4 mils. While there is greater uniformity in cell structure than that in Fig. 3, the particle boundaries, both fused and unfused to each other, are more apparent because of consistently small cells at the surface. This is also apparent in the boundaries shown in the X30 photomicrograph. The X170 view again shows the strut-and-window pattern.

In Fig. 5 is shown the X5 view of a foam structure that, for polystyrene, is exceptionally small and uniform with cells in the 2 to 4-mil diameter range. However, other heterogeneities are apparent in this photograph - first, an imperfect welding of several particles to each other, and second, an erratic occurrence of from none to four voids of 10 to 25-mil diameter. These voids are believed to originate from water droplets. The X30 view depicts the extremely fine surface cells. In the X170 view the struts of this very small-celled foam appear to be thinner than those of the large-celled foams of Fig. 3 and 4.

In Fig. 6 is the X5 view of a cell structure showing the heterogeneities that can occur when a certain raw material has not matured sufficiently

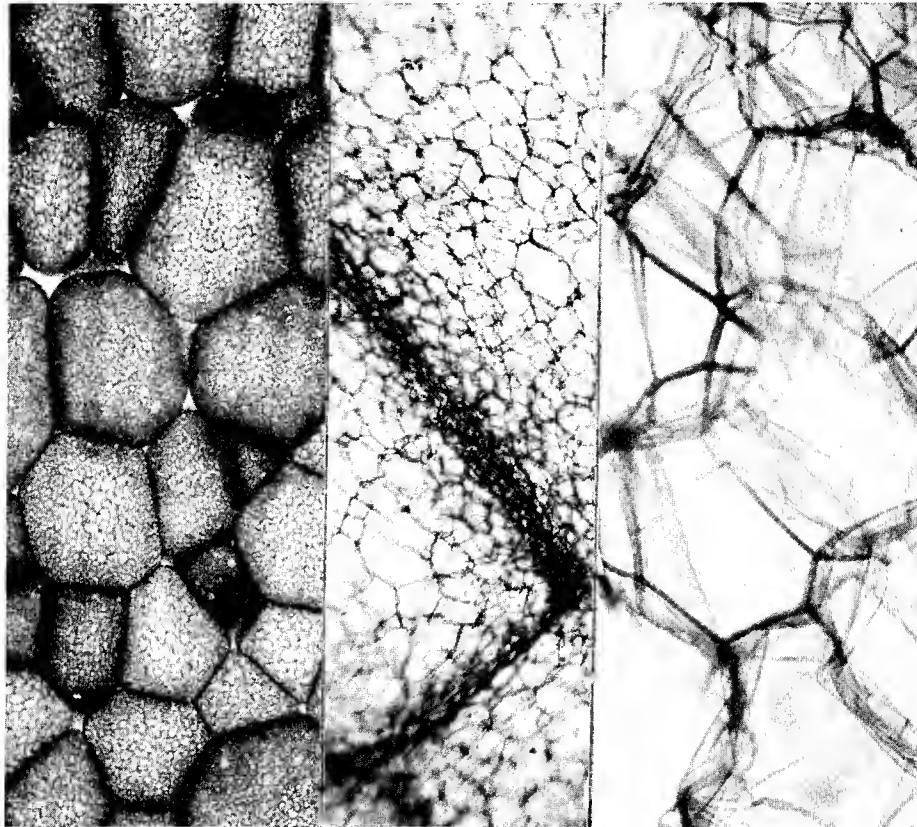


Fig. 4---Molded Bead Foam B, 1.0 lb/ft³ (X5, X30 and X170).

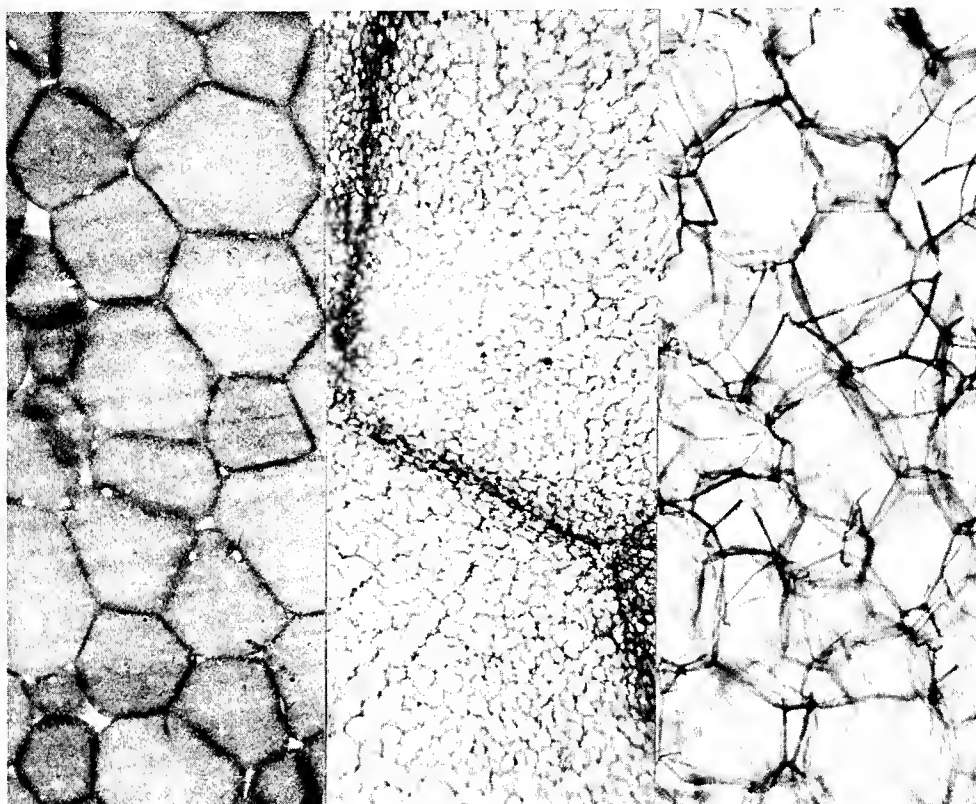


Fig. 5---Molded Bead Foam C, 0.9 lb/ft^3 (X5, X30 and X170).

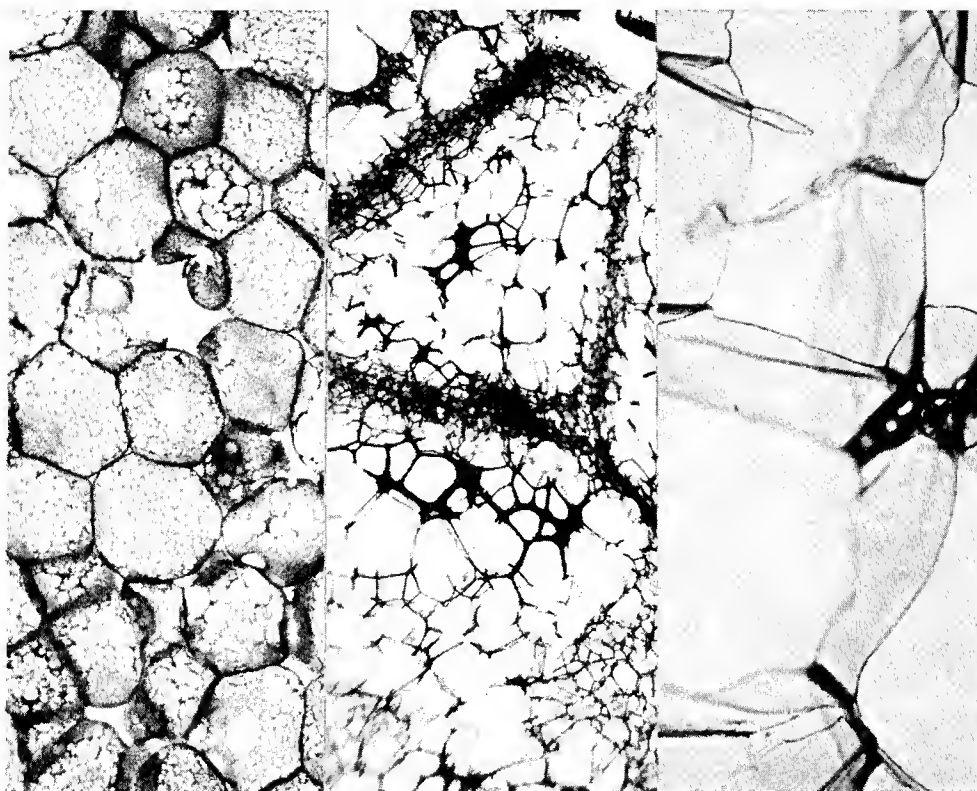


Fig. 6---Molded Bead Foam D, 1.0 lb/ft³ (X5, X30 and X170).

before expanding. While one particle appears to be a hollow sphere and some particles have very large cells (to 38 mils in diameter), others exhibit cells of 4 to 8-mil diameters. Many particles have shells of very fine cells. The shell effect is especially apparent in the X30 view, showing a shell of 1 to 2-mil cells covering a foam of about 8 to 17-mil cells. In the X170 view is a cell of about 12 x 16-mil dimension. The struts are obviously thicker than those of the smaller celled foams shown previously.

In Fig. 7 is the X5 magnification of a foam with 2 to 4-mil cells in all particles, some of which have interiors with 6 to 8-mil cells, and some of which have zero, one or two voids in the 25 to 38-mil range. Of particular interest is the fact that the particle boundaries show very little densification or smaller cell structure - an observation supported by the X30 magnification. The boundaries appear to be formed from the fusion of a single layer of 2 to 4-mil cells at the surface. Such foams exhibit a completely random pattern of rupture when torn. In the X170 view is a region of cells with about 4-mil diameters, showing a pattern of thick struts with extremely thin windows.

In Fig. 8 is seen a material consisting of small-celled (2 to 6-mil diameters) foam "peppered" with voids of about 8 to 10 mils. Nearly every particle also contains a crater, apparently left by a bubble of escaping vapor as the particle was hardening during manufacture. (It is not possible in a cross section to show the crater in every particle.)

In Fig. 9 is seen an extruded board foam. The density of this product is 1.8 lb/ft³, whereas the foams shown previously were in the range of 0.9 to 1.3 lb/ft³ in density. The cells are larger, 25 to 50 mils, than those of the bead foams, but because of the lack of particle boundaries, the extruded foams present a uniform appearance. At the higher magnifications, X30 and X170,

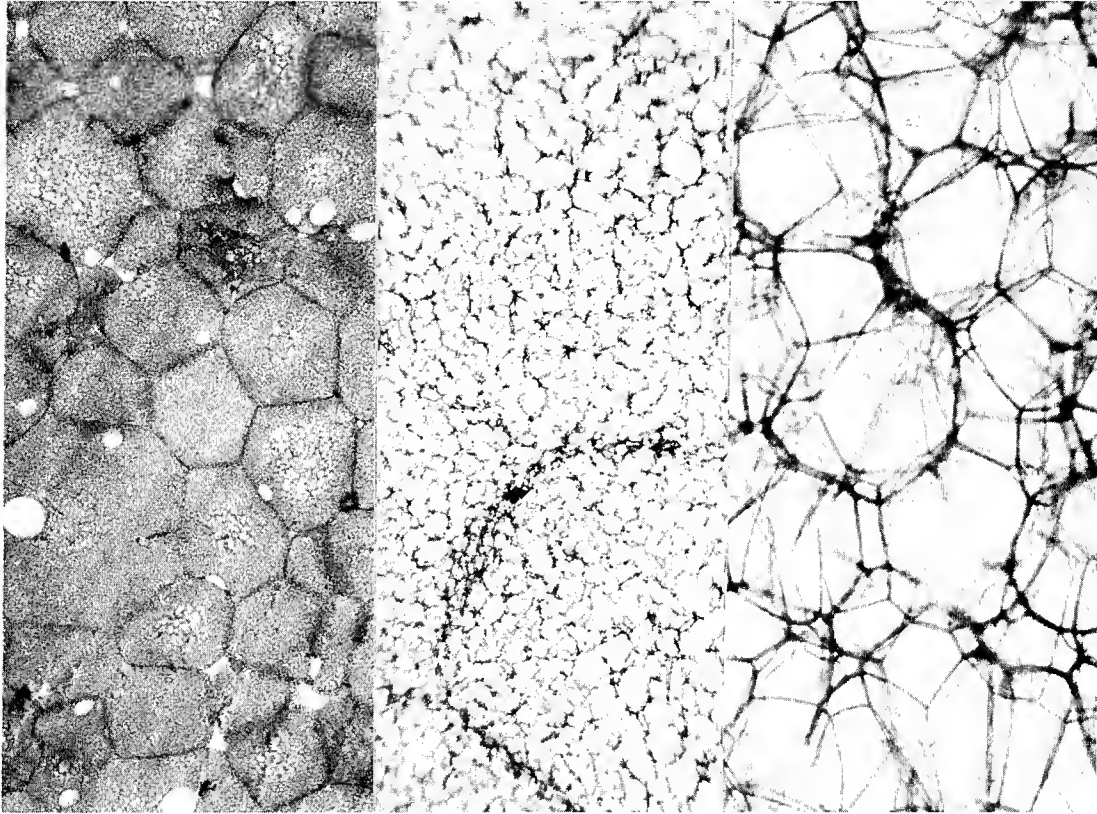


Fig. 7---Molded Bead Foam E, 0.9 lb/ft^3 (X5, X30 and X170).

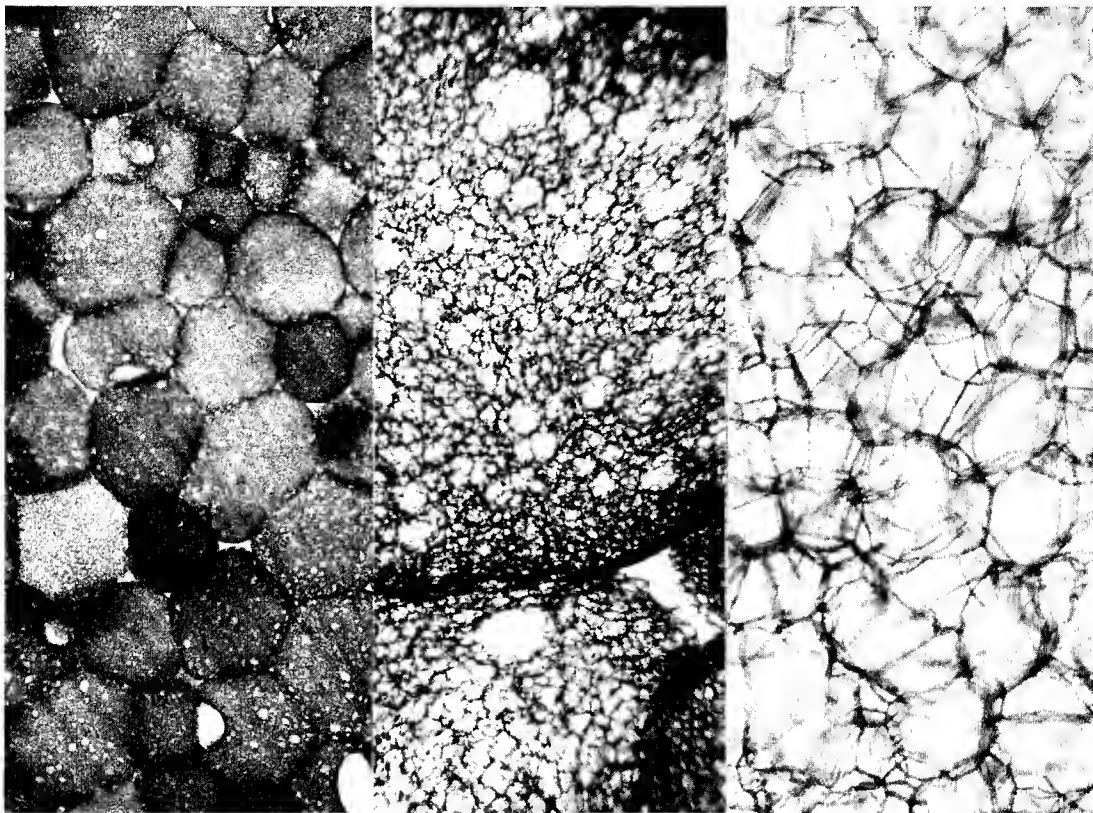


Fig. 8---Molded Bead Foam F, 1.0 lb/ft³ (X5, X30 and X170).

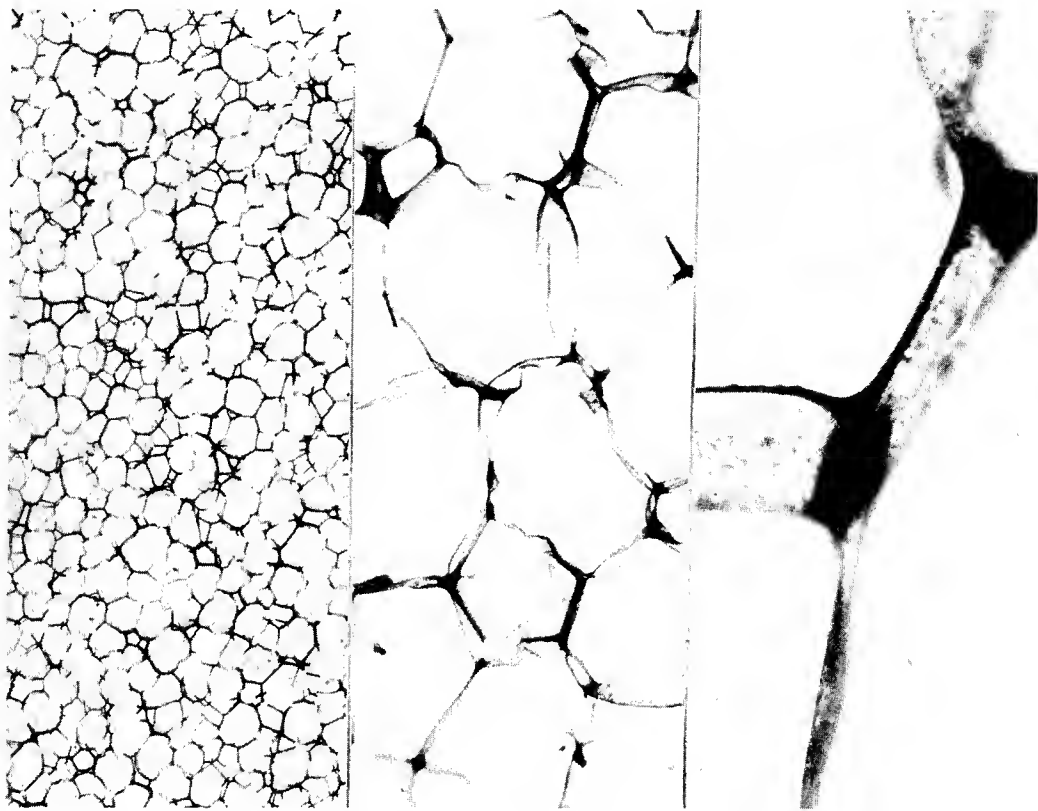


Fig. 9---Extruded Board Foam, 1.8 lb/ft³ (X5, X30 and X170).

the strut-and-window patterns are apparent but not as pronounced as in the bead foams.

Extruded Sheet

Two types of extruded polystyrene sheet are considered - the so-called "low" and "medium" density types of about 4 to 6 and 12 to 20 lb/ft³, respectively. Both varieties are produced by an operation similar to that of making polyethylene film, i.e., the blowing of a tube of hot plastic as it emerges and expands from the circular die of an extruder. Sheets of polystyrene foam are thermoformed into consumer products such as containers, trays and packages from the low density foam and beverage cups from the medium density foam.

In examining the cell structure of extruded foams it is important to observe the skin as well as the extent of flattening of the foam cells by the air pressure inside the tubular extrudate. To study this effect, one obtains a so-called "cross-machine" specimen from which to view the cut edge of a cylinder of extrudate. It is also important to obtain an "in-plane" view by "looking through" the sheet. This view, perpendicular to that of the "cross-machine", permits one to determine if any orientation has been introduced by pulling the foam.

Specimens of extruded foams were cut by a razor blade until one of the desired size, uniformity and thickness was obtained. For the "in-plane" specimens, the skin of a small area, about 1 cm², was first cut away. The sections were mounted between two glass microscope slides, caution being taken not to crush the sections. Photographs were taken at two magnifications: X28 via a 35-millimeter photographic enlarger, using the mounted section as a negative; and X170 via a microscope.

Figure 10 depicts X28 and X170 magnifications of cross-machine views of a relatively fine-celled, satin-textured, non-brittle sheet of a density of 5 lb/ft³ and a thickness of 80 mils. The X28 photograph shows both edges of the sheet, indicating no densification of one surface and a slight densification of the other. The X170 photograph plainly shows the flattening effect of air pressure on the cells, since many of the "holes" are 3 mils in width and 9 to 10 mils in length. In the in-plane view of X28 magnification in Fig. 11, very little distortion is seen from the perpendicular forces of air compression or lateral force of wind-up tension. The windows measure about 7 mils in width. In the X170 photograph can be seen a nearly complete cell, measuring about 12.5 mils at greatest diameter.

In Fig. 12 are shown the "cross-machine" and "in-plane" cell structures at X28 magnification of a coarse-celled, brittle polystyrene foam sheet. Such coarse foam can result from a deficiency of cell-nucleating agent and/or an excessively high extrusion temperature. In the "cross-machine" view, the cells measure 11 to 14 mils in width and 18 to 25 mils in length, while in the "in-plane" view the wall-to-wall distance is between 14 and 18 mils.

A foam sheet in the so-called medium density range, in this case 20 lb/ft³ and 105-mil thickness, is shown in the "cross-machine" view at X28 and at X170 in Fig. 13. Such foams are made with a lower quantity of blowing agent than the 5 lb/ft³ foams shown previously. At the surface of the foam is seen a dense skin which was created deliberately to enhance the utility of the material for making cups that can be stacked in a vending machine. Figure 14 represents the in-plane views at X28 and X170 magnification of the interior of the same medium density sheet. It is noted that this foam has a "Swiss-cheese" cell structure, rather than the strut-and-window structure of all other foams.

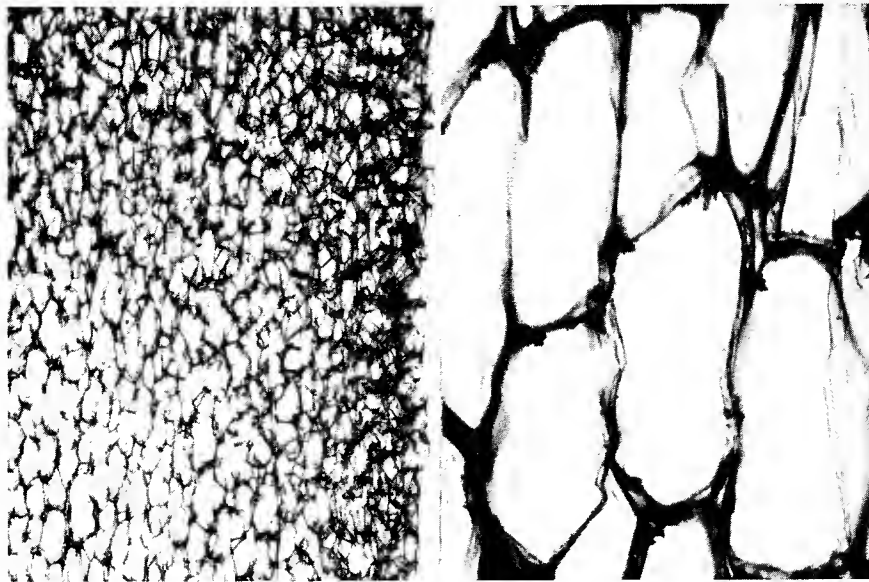


Fig. 10---Extruded Fine-celled Sheet, 5 lb/ft³, in Cross-machine View (X28 and X170).

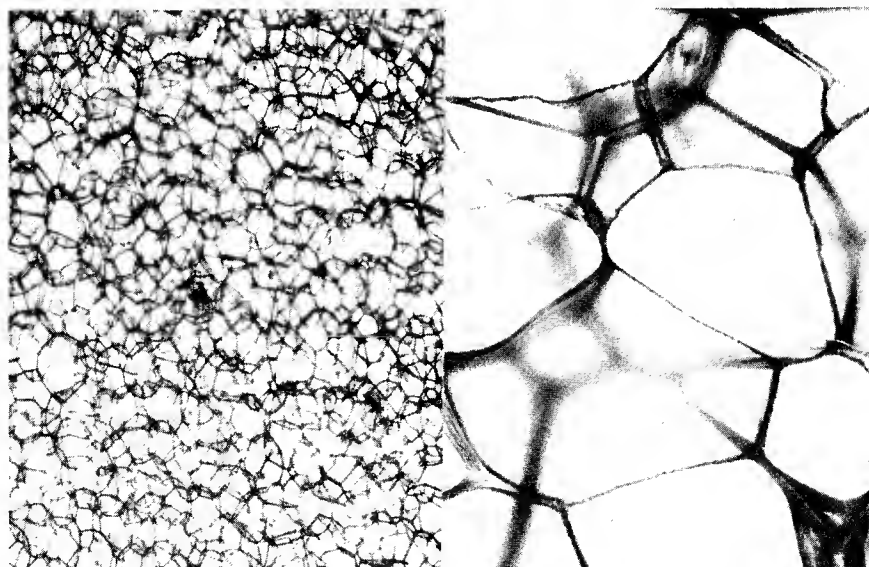


Fig. 11---Extruded Fine-celled Sheet, 5 lb/ft³, in In-plane View (X28 and X170).

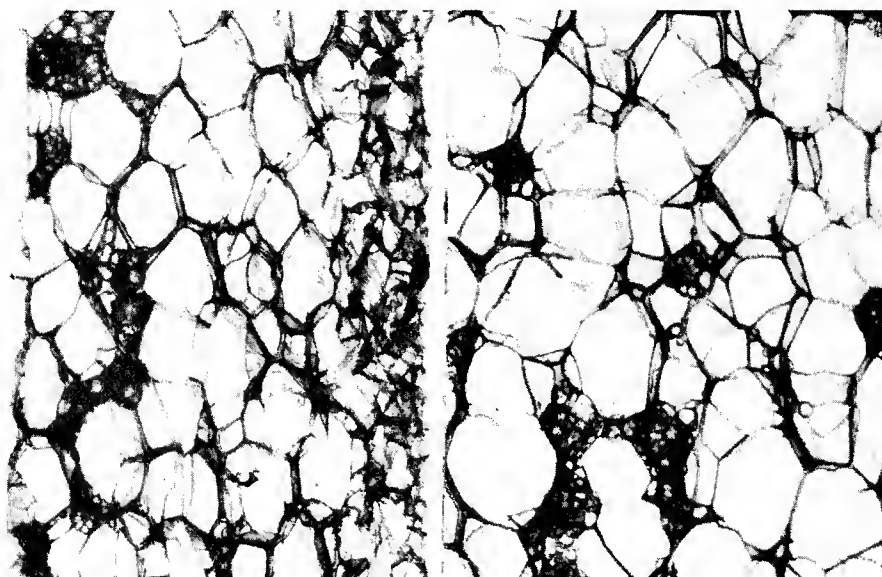


Fig. 12---Extruded Coarse-celled Sheet, 5 lb/ft³, in Cross-machine
and In-plane Views (X28).

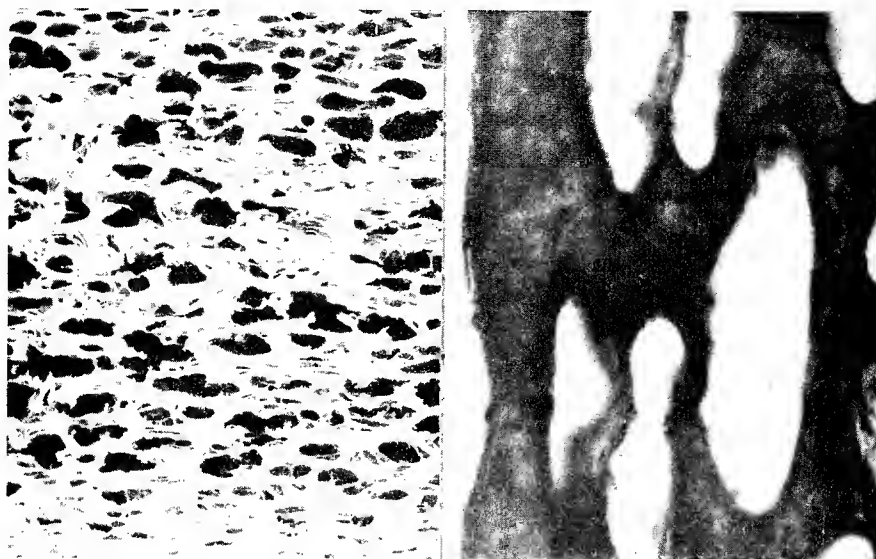


Fig. 13---Extruded Sheet, 20 lb/ft³, in Cross-machine Views (X28 and X170).

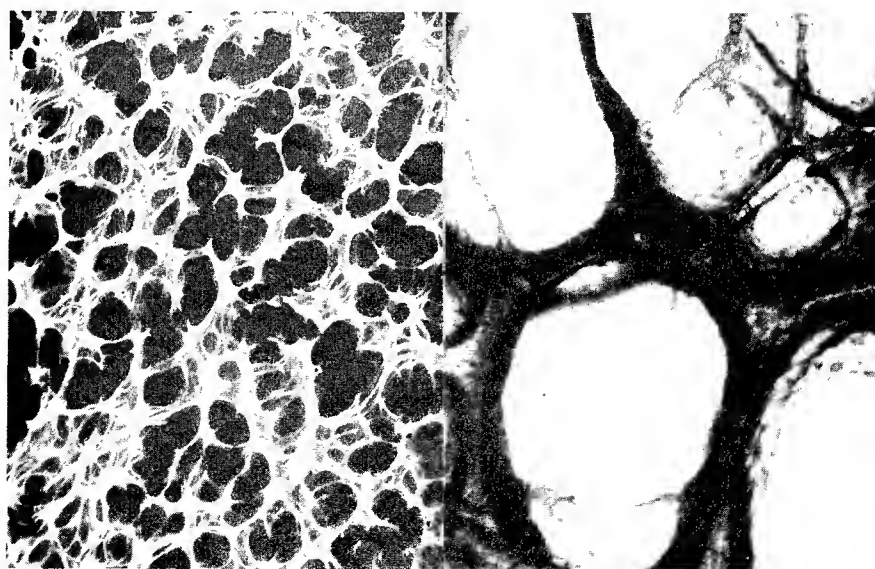


Fig. 14---Extruded Sheet, 20 lb/ft³, in In-plane Views (X28 and X170).

Electron Microscopy

Non-molded expanded beads with a bulk density of 1 lb/ft³ were examined in the electron microscope at the skin and the interior. Pieces of the skin were peeled off, with the aid of a pair of sharp-pointed forceps, in strips of about one-mil thickness. Slices of two-mil thickness were cut from void-free locations in the interior, using a fresh razor blade. Specimens with an area of about 2 mm² were sandwiched between two sample grids, without substrate, mounted in a sample holder. Micrographs taken at approximately X4,000 were enlarged to a total magnification of X33,700 in a photographic enlarger. Replica methods were not used since the foam fragments were thin enough for direct examination.

Two types of foams were chosen for this study - one with a cooling time in 20 x 20 x 12-inch molds of 3 to 5 minutes and the other with a cooling time of 18 to 20 minutes - because of the possibility that the nature of the cell windows might influence the cooling time. Figure 15, depicting the fast-cooling foam, shows that the cell windows at the surface as well as the interior of the foam are heavily veined with areas (appearing dark in the photograph) transparent to the electron beam. Figure 16, depicting the slow-cooling foam, shows that the surface is substantially opaque while a cell window at the interior exhibits some semi-transparent veins and scattered holes. It is believed that the veins (of about 0.05-micron width) are areas of polystyrene film which have been excessively stretched during expansion. Since diffusion of vapor through the veins should be more rapid than through the thicker opaque areas, it seems logical that the cell walls with more of such areas should exhibit a more rapid loss of pressure (as well as temperature) during the foam-cooling phase of molding of bead foams.

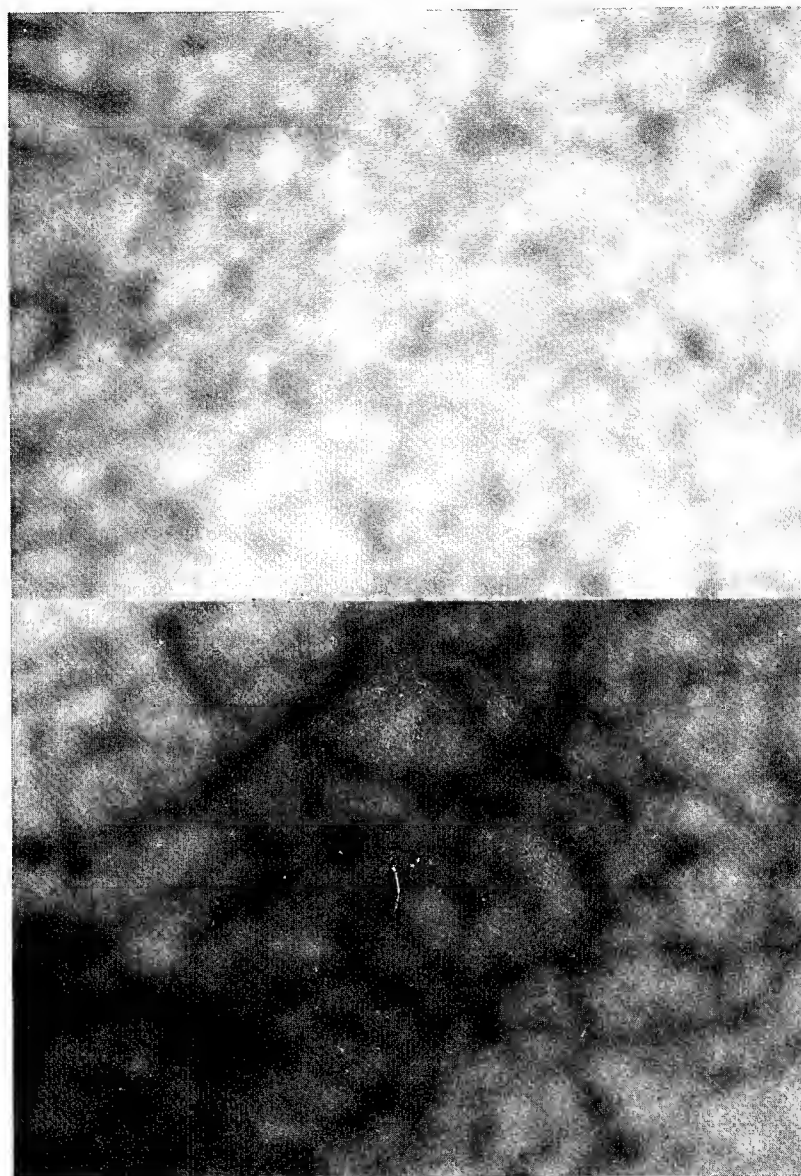


Fig. 15---Electron Micrographs of Cell Windows at Surface (top) and Interior (bottom) of Expanded Beads of Fast-cooling Foam at a Bulk Density of 0.96 lb/ft^3 (X4,000 Enlarged to X33,700).

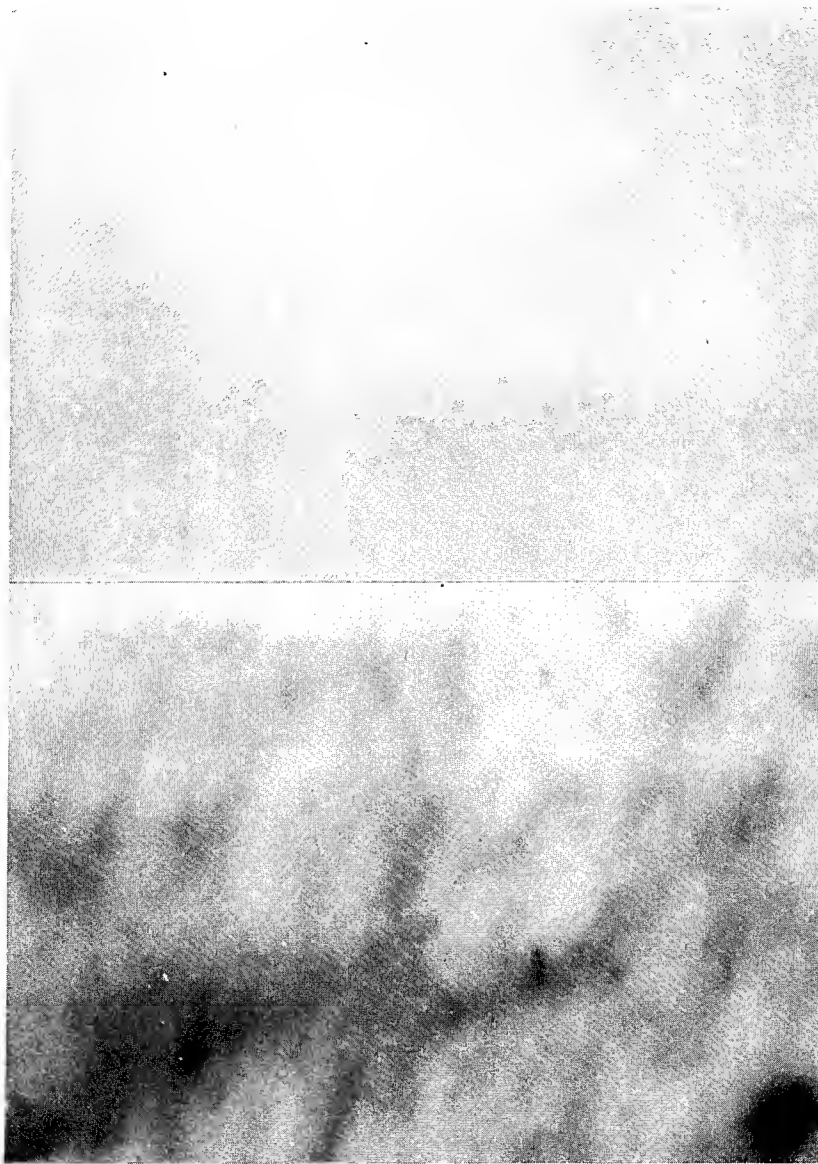


Fig. 16---Electron Micrographs of Cell Windows at Surface (top) and Interior (bottom) of Expanded Beads of Slow-cooling Foam at a Bulk Density of 1.2 lb/ft^3 (X4,000 Enlarged to X33,700).

The Expansion Process

We shall now review some small-scale investigations intended to give us a better understanding of the formation of these foam cells. As seen in Fig. 17, beads are pre-expanded using a household double boiler with a sample supported on a 100-mesh screen in the cut-out bottom of the upper pan while steam is generated from boiling water in the lower pan. We may also use a bath of boiling water or a chamber filled with steam from a line source as the environment for expansion. Typical expansion rates for three types of polystyrene expanded by n-pentane are shown in Fig. 18, in which the bulk density of the foam particles is plotted against time in minutes. The only variable here is in the molecular weight of the polymer, as indicated by the intrinsic viscosity values on the three curves. We see that expansion rate, ultimate expansion and collapse of the foam in steam at 100°C are greatly influenced by molecular weight. The curve at the top represents that of a high-strength, injection-molding grade of polystyrene. While expansion is relatively sluggish, this type of foam has a high resistance to shrinkage from prolonged steaming at elevated pressures as well as atmospheric pressure. The bottom curve is obtained from a rather brittle polystyrene with barely adequate physical properties. While this material expands very rapidly, the foam collapses at about three minutes of exposure to atmospheric steam. The commercial expandable polystyrenes exhibit curves which fall between these two limits.

By measuring cell size as a function of foam density, Pogany concludes that all cells form simultaneously at the beginning of expansion and then increase in size without coalescence or rupture at least within normal conditions of expansion in steam at 100°C (5).

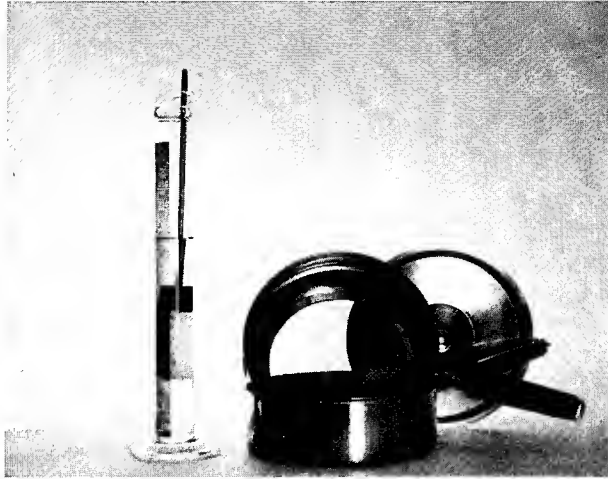


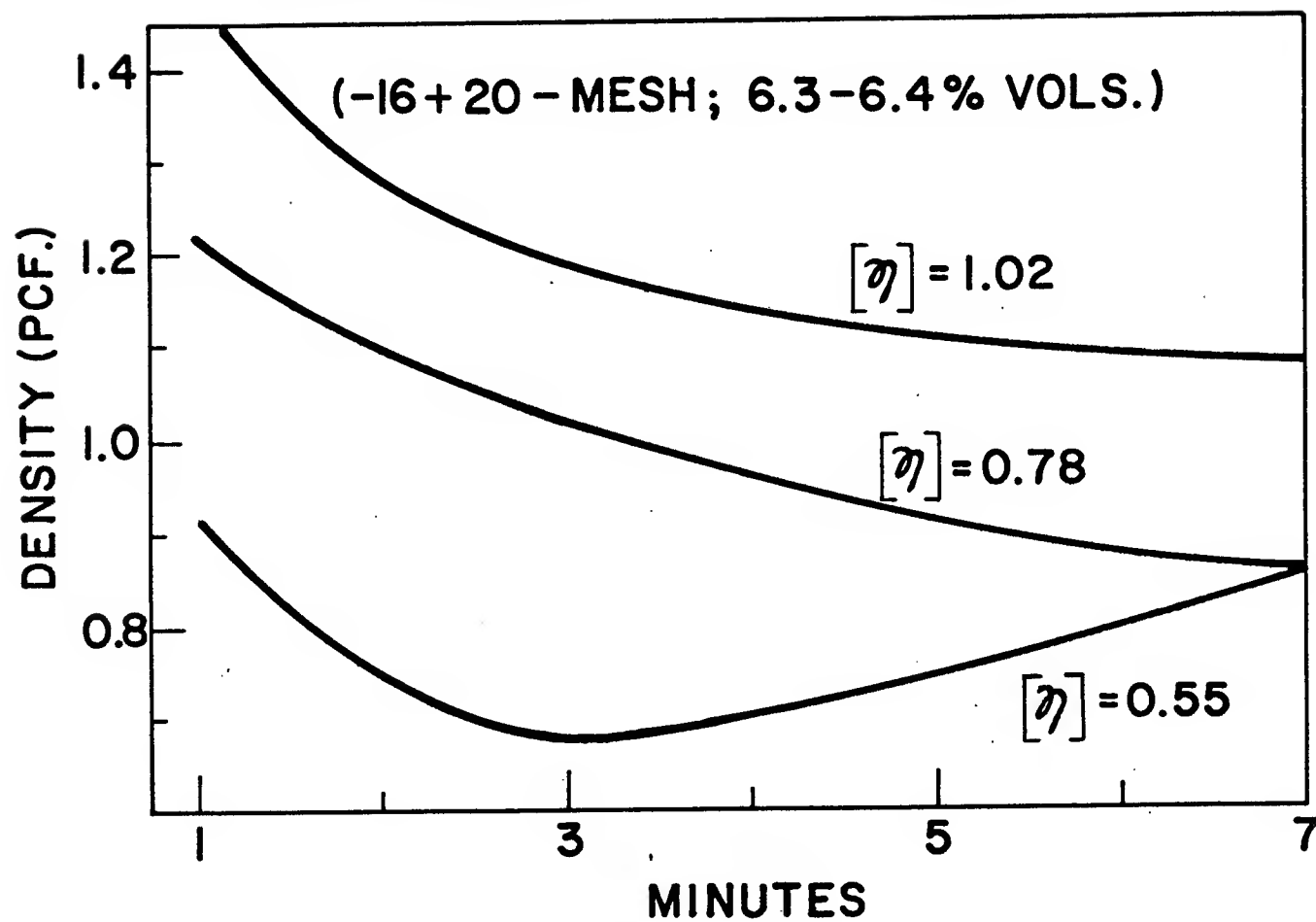
Figure 17

Left: Density measurement from water displaced by 1.0 gram of prepuff. Bulk density = measured density x 0.59.

Right: Laboratory pre-expander made from household double boiler with 100-mesh stainless steel screen inserted in the top pan.

Figure 18

EXPANDABILITY VS. MOL. WT.



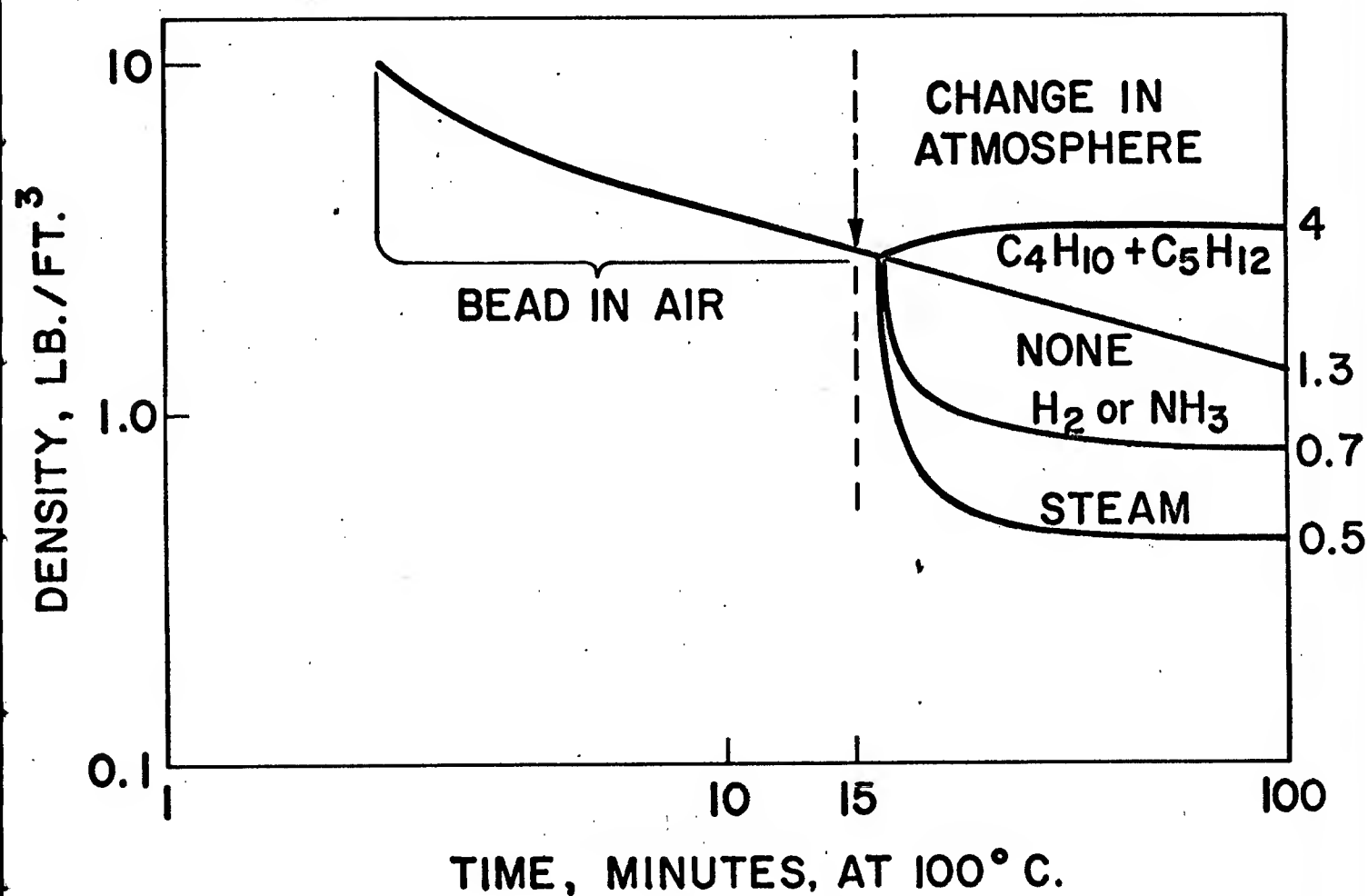
The question may be asked, "How do these expansions compare with the theoretical value one might obtain from pentane alone, assuming no loss of vapor and no restriction by the polymer to expansion?" Surprisingly, such theoretical densities are quite high, about 1.4 pcf. in bulk density. How fortunate we are to be able to get twice as much expansion out of polystyrene as the blowing agent will allow. What else, then, is assisting us as a blowing agent? The answer is that air and steam permeating the expanding beads act as auxilliary blowing agents. It must be realized that the internal pressure of pentane offers no restriction to the incoming permeation of air and steam. Their permeation is affected only by the partial pressure of air and steam inside the cells. Excellent experimental proof of this effect is shown in Fig. 19 (6). The expansion of a single bead impaled on a needle at 100°C was observed. Expansion was permitted for 15 minutes to a density of about 3 pcf., then the atmosphere was changed completely. You will note that in the case of steam the density dropped abruptly to below 1 pcf. and ultimately to 0.5 pcf. in 100 minutes. Without changing the atmosphere, the density reached only 1.3 pcf. If the atmosphere was changed to hydrogen or ammonia, the ultimate density was about 0.7 pcf., while a change to an atmosphere of a mixture of butane and pentane produced essentially no further expansion.

It seems obvious that expandability should be improved by adding more blowing agent. Figure 20 indicates there is a limit to the amount of n-pentane which can be utilized for expansion. Since the 3-minute, 5-minute and 7-minute curves of foam density vs. n-pentane content do not parallel each other, we can assume that it is because the excess pentane is being wasted by evaporation early in the expansion process. Also, at 7 minutes, there is little difference in the density of foam generated from 6 to 8% of n-pentane. We see in Fig. 21

Figure 19

EXPANDABILITY VS. ATMOSPHERE

(SKINNER, BAXTER and GREY)^{a)}



^{a)} PLASTICS INST. (LONDON) TRANS. J., 32, NO. 97, 180 (1964)

Figure 20

EXPANDABILITY VS. VOLATILES

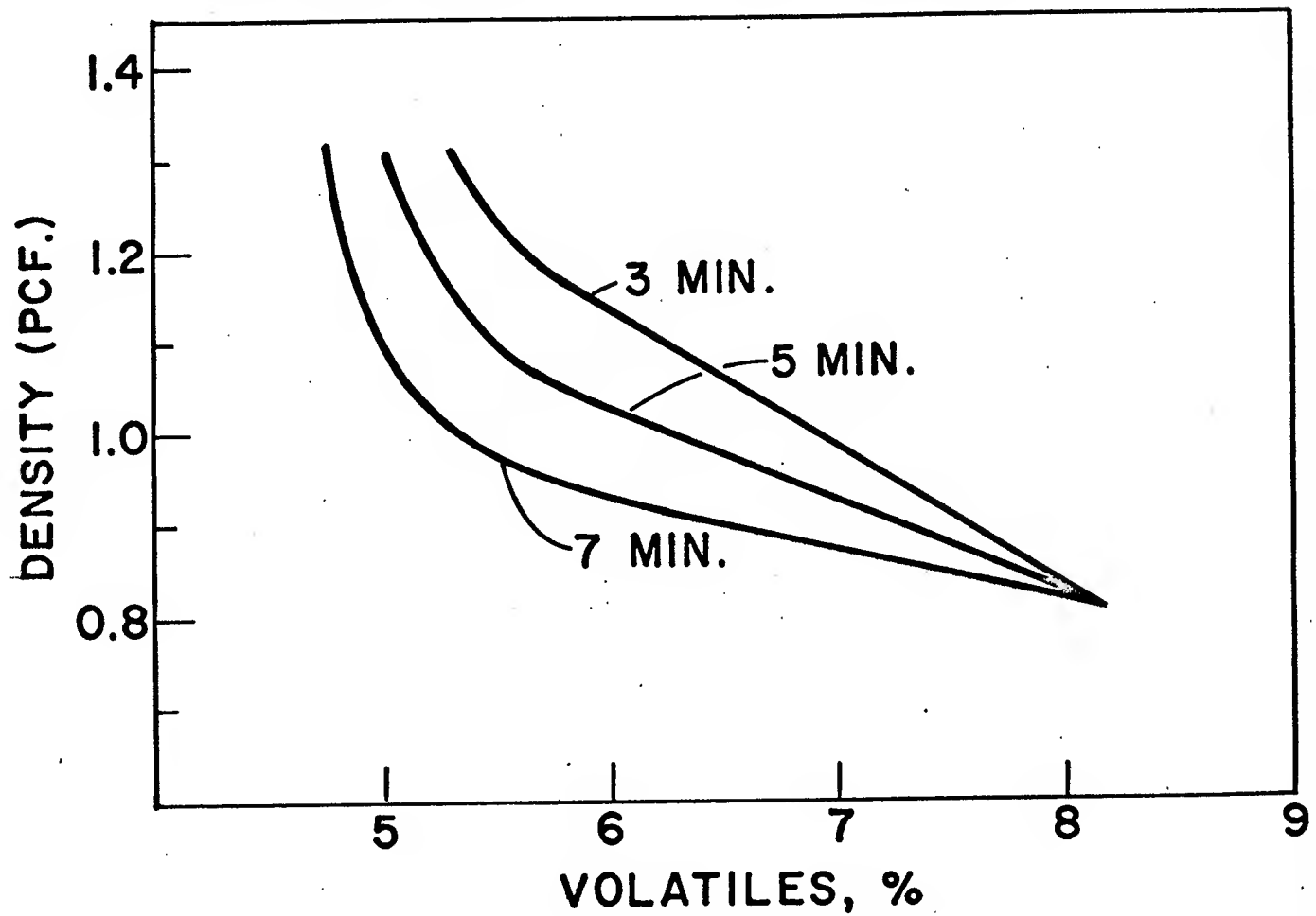
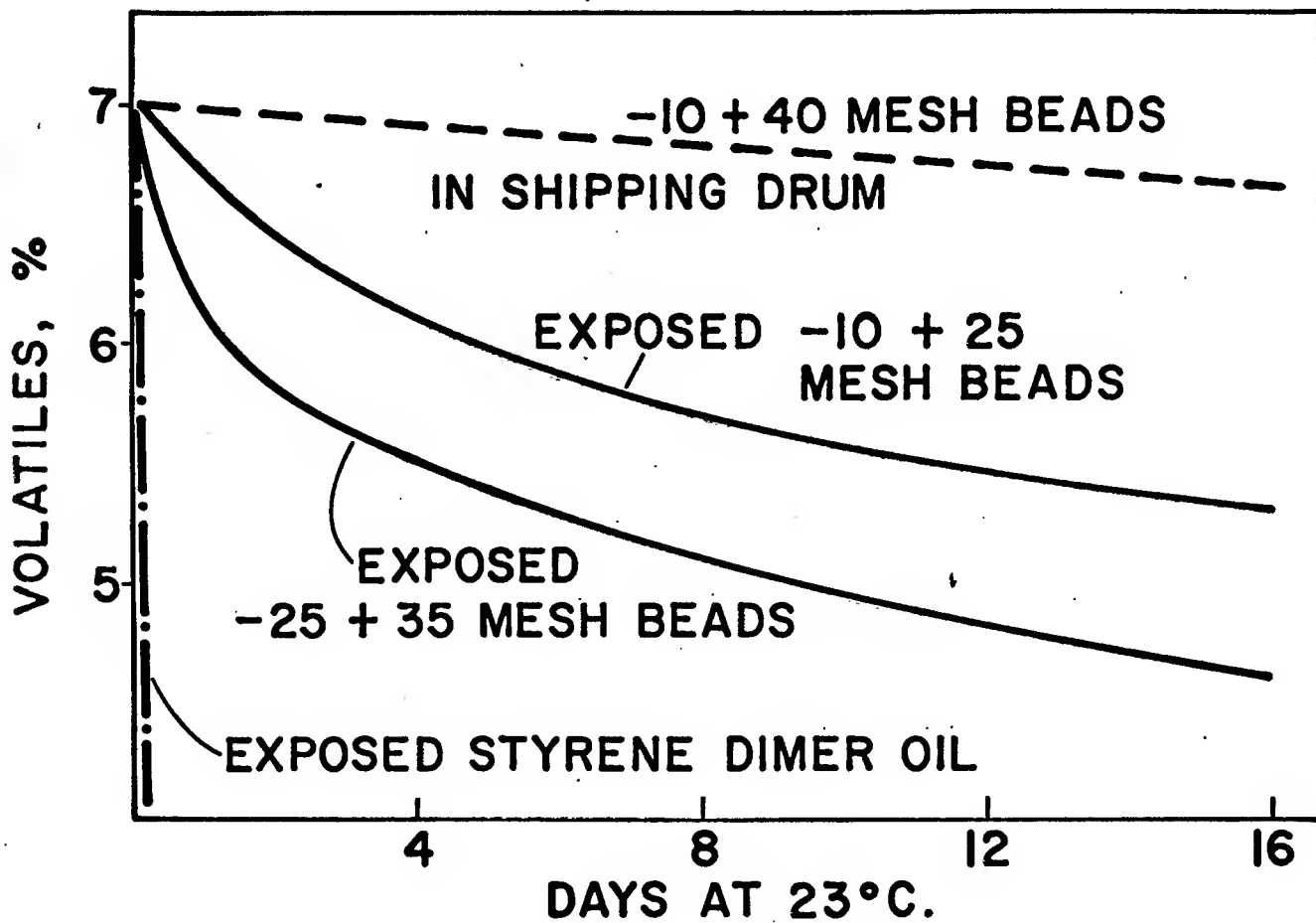


Figure 21

n-PENTANE LOSS FROM POLYSTYRENE



that at 7% pentane there is a steep slope in the weight loss curve of exposed beads of either board-molding or cup-molding size. Also, the smaller beads lose the blowing agent much faster than the bigger beads unless a pentane pressure is maintained in the container, as shown in the top curve. The curve at the left is especially interesting for theoretical reasons because it represents a true solution of pentane in a liquid polystyrene - a dimer of styrene monomer. This behavior of extremely rapid loss of pentane from the polystyrene oil suggests that in the solid polymer there are much stronger retentive forces in operation than those acting between two liquids. Figure 22 shows another reason why excess pentane should be avoided, in that enlarged cell size is obtained which cannot be corrected by aging of the beads. Apparently, the excess of pentane did irreparable harm to the cell structure.

If we place isopentane, with a branched molecule, in polystyrene beads, we find, as seen in Fig. 23, that it is retained more strongly than n-pentane which has a linear molecule. This retention occurs in spite of the fact that isopentane is much more volatile, boiling at 28°C, whereas n-pentane boils at 36°C. It is also observed that the cells of isopentane-expanded foams are smaller than those of n-pentane-expanded foams when the expandable beads are made in an identical manner.

Having seen the effect of changing blowing agent in polystyrene, let us change the polymer and use n-pentane as a common blowing agent. In Fig. 24 are presented weight loss curves for polyethylene, polystyrene and a styrene/acrylonitrile copolymer. It is apparent that those polymers which exhibit the fastest weight loss also have the largest cell size in their foams. An interesting observation with polyethylene is the fact that it does not hold

Figure 22

CELL SIZE VS. VOLATILES AND AGE

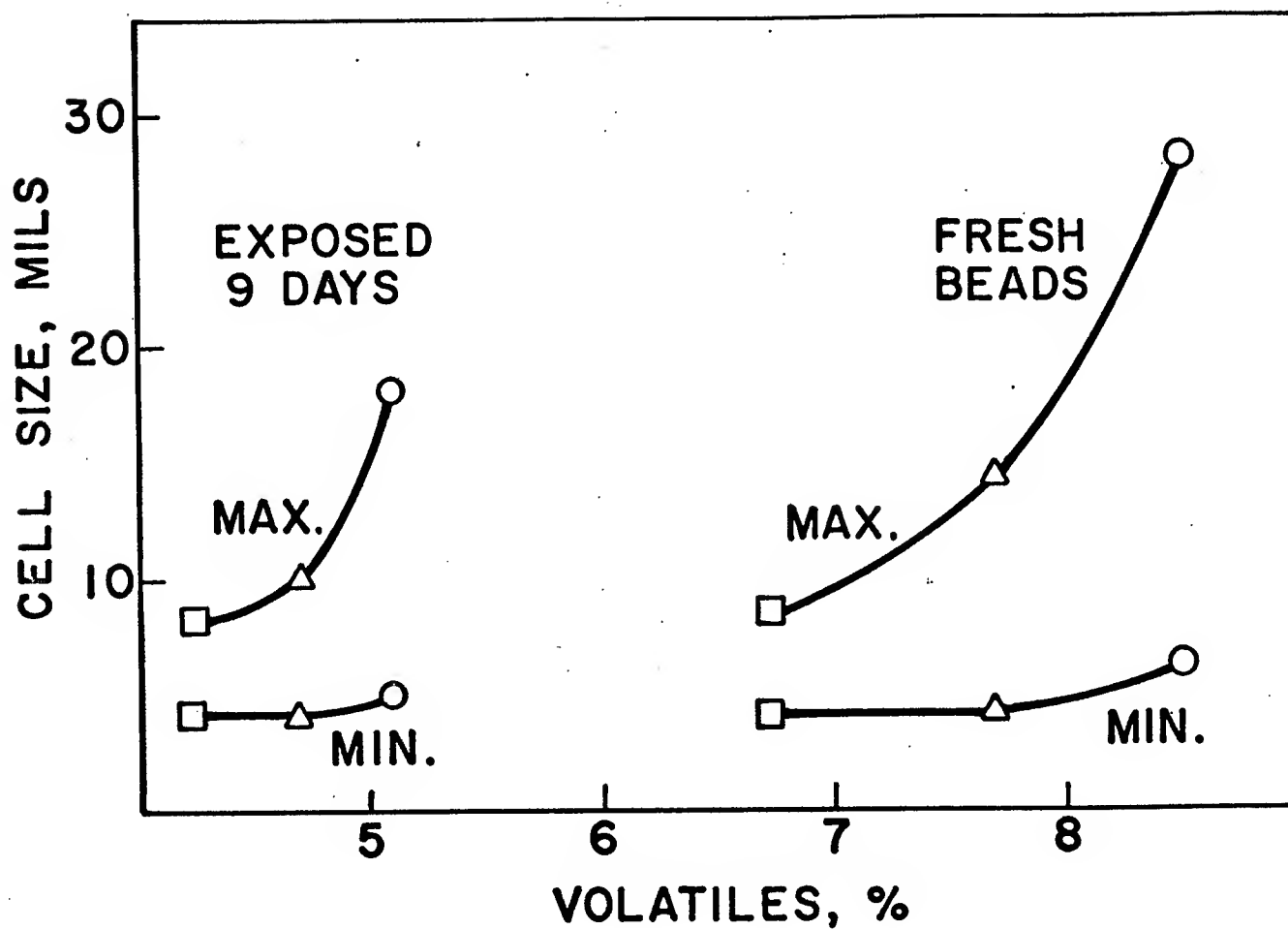


Figure 23

HYDROCARBON LOSS FROM POLYSTYRENE BEADS

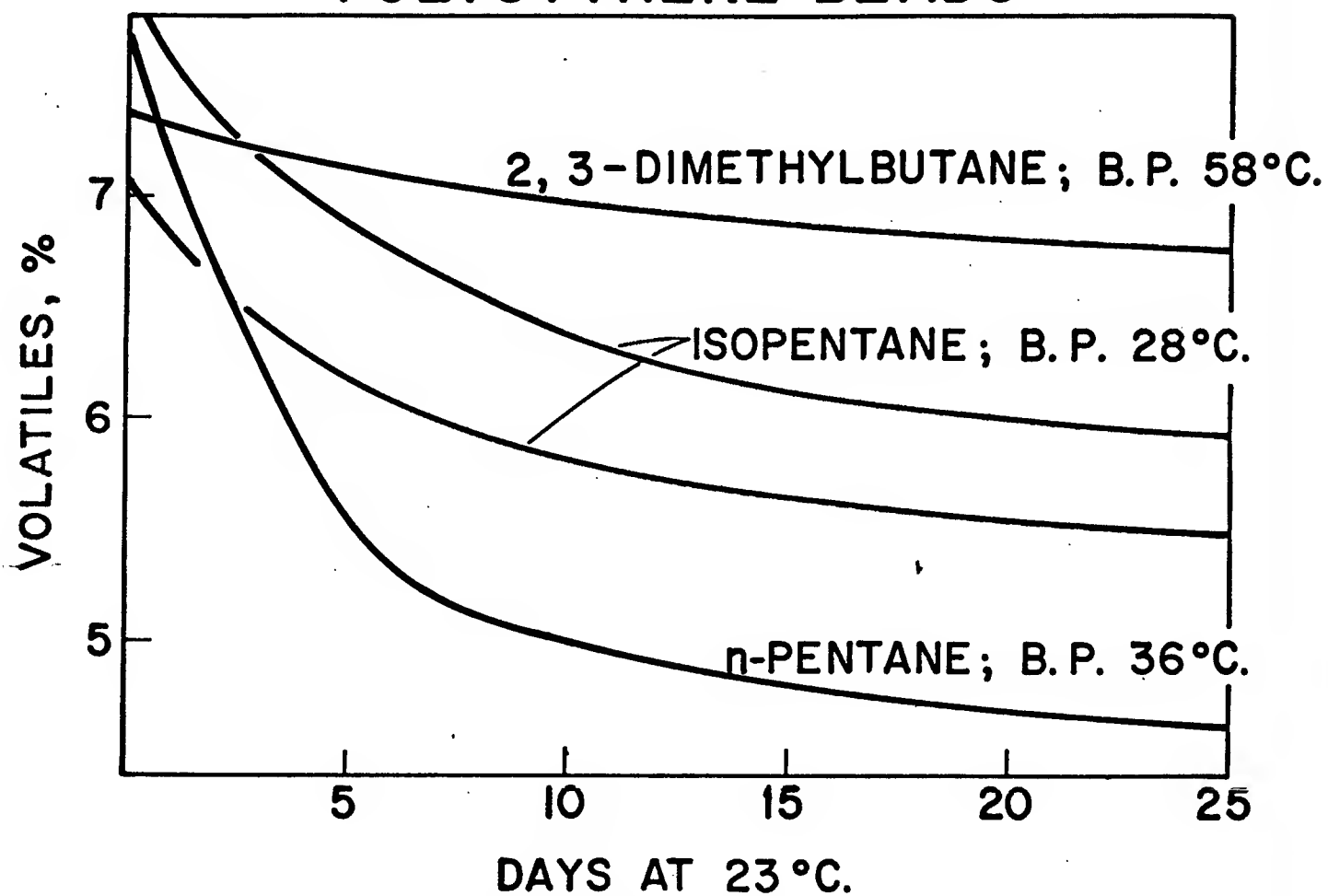
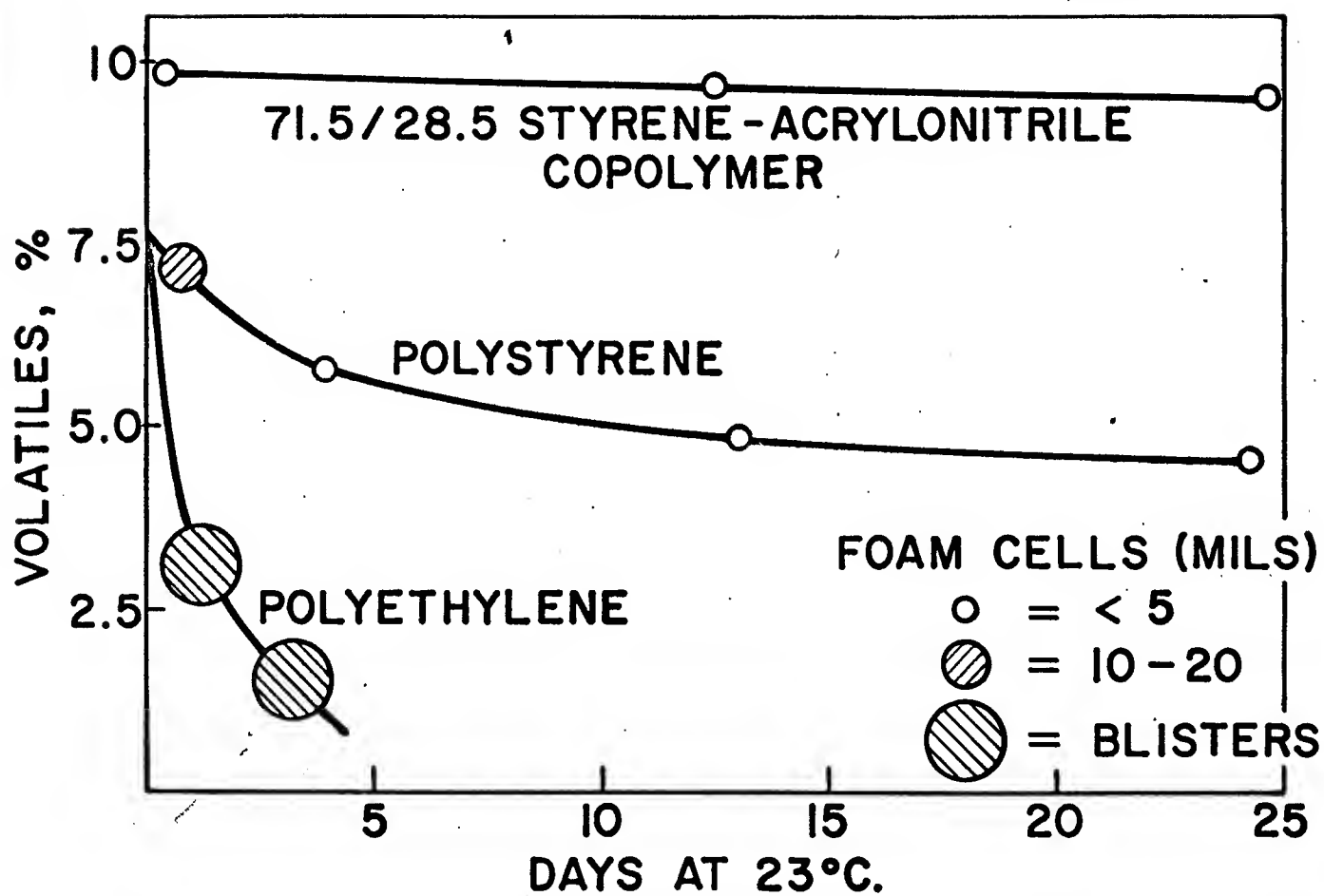


Figure 24

n-PENTANE LOSS VS. POLYMER



pentane any better than mineral oil holds pentane. This is not too surprising when we realize that in the amorphous regions of polyethylene the molecules are free to move, while in polystyrene the molecules are frozen up to about 100°C, the second-order-transition temperature. In the copolymer the molecules are not only frozen, but are attracted by strong intermolecular polar forces between the acrylonitrile portions, thus making it possible to accommodate much higher amounts of pentane without harming shelf life or cell structure.

Such observations led us to consider how pentane is distributed among the chains of polystyrene. Does pentane occupy cages that already exist in a polystyrene matrix or does it push the chains apart? In other words, is polystyrene "packed" with pentane or is it swollen by pentane? Excellent support for the cage-filling structure of expandable polystyrene was recently published (7). According to Haward, who extrapolated to zero internal pressure the polystyrene compressibility data of Breuer and Rehage, the free volume frozen into polystyrene at its glass transition temperature is 13%, not 2.5% as had been taken for granted for all thermoplastics for many years. In Fig. 25 are compared three different methods of deriving the free volume in polystyrene. A value of 17% is obtained by methods of Biltz, who calculated the closest packing of molecules, based on a study of liquids (8). The method generally accepted for thermoplastic polymers is the third one, originally proposed by Williams, Landel and Ferry in 1955 (9). This method, based on viscosity and the thermal coefficient of expansion, gave a value of about 2.5% for a variety of cellulose, rubbers and methacrylates.

If we calculate the amount of n-pentane which can be packed into polystyrene at the glass temperature, a free volume of 13%, according to Haward, gives a limit of 6.5% by weight (extrapolating the density of n-pentane to be

Figure 25

Free Volume and Pentane in Polystyrene

<u>Determination of Free Volume</u>				<u>n-C₅H₁₂</u>
<u>Method</u>	<u>T, °C</u>	<u>Free Vol., %</u>	<u>g/cc Max.</u>	<u>Capacity Wt. %</u>
Compressibility ^{7/}	100	13	1.18	6.5 est.
Mol. Structure ^{8/}	100	17	1.22	8.5 est.
Visc.; ΔV vs. T ^{9/}	100	2.5	1.07	1.3 est.
Expandable Polystyrene	25	14*	1.22**	7.5 obs.

$$* = \frac{(0.075)}{(d_{C_5H_{12}})} \times [(100)(d_{ps}) + (\% \text{ FV})(d_{C_5H_{12}})]$$

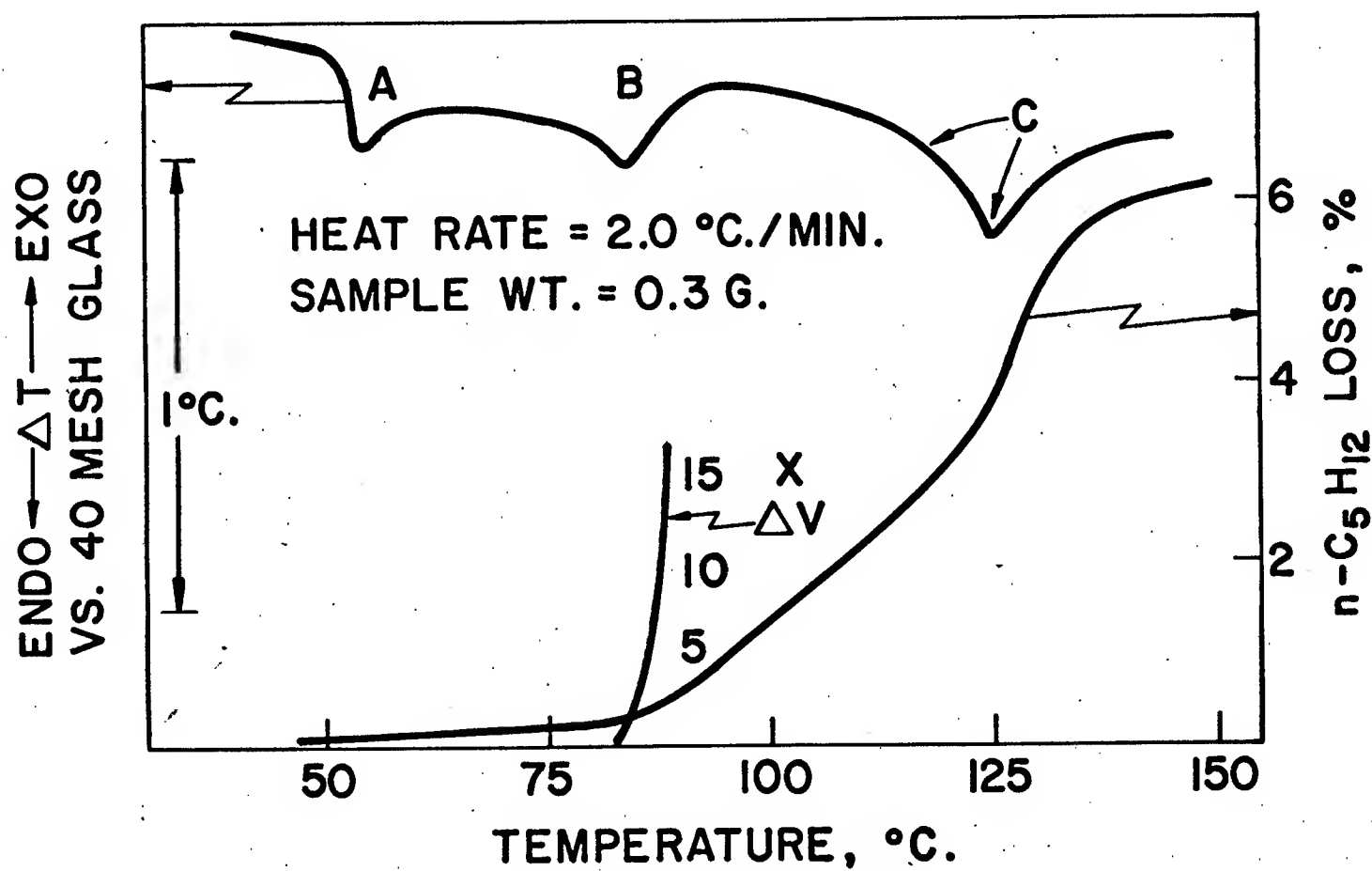
$$** = \frac{d_{ps}}{1.00 - \%FV/100} = \frac{1.05}{1.00 - 0.14}$$

0.55 g./cc at 100°C). The free volume of 17% from Biltz gives 8.5% n-pentane, while the classical value of 2.5% gives only 1.3% n-pentane. Actually, the limiting amount of n-pentane in high molecular weight polystyrene is about 7.5%, since the presence of higher amounts leads to excessive evaporation rates, very soft polymer and blistered, shrinking foam. If 7.5% n-pentane does occupy the limit of the free volume, then the authentic free volume is calculated to be 14% at room temperature. This is in good agreement with Haward's calculation for the glass transition point. There is supposed to be little or no change in free volume with temperature below the glass temperature, provided there is no crystallization.

The next topic we wish to consider is a study of the various phenomena that occur upon heating of expandable beads at a constant rate. Figure 26 shows data obtained by L. C. Couchot of our Physical Chemistry Group on Dylite^(R) F-40 beads. The upper curve is the so-called DTA (differential thermal analysis) curve because it compares the difference in temperature between 0.3-gram samples of 40-mesh glass beads and expandable polystyrene beads of similar size. Both samples were heated simultaneously in an aluminum block, the temperature of which was raised at a rate of 2°C per minute. If no heat were absorbed or evolved by the expandable polystyrene, a straight line would result. However, if the curve dips down, heat is being absorbed and an endothermic process is occurring. Melting and evaporation are endothermic processes. The upright curve in the middle of Fig. 26 is the expansion curve obtained on a hot-stage microscope, while the bottom curve is the so-called thermogravimetric analysis (TGA), which is a weight-loss curve, obtained by supporting the heated sample from the beam of an analytical balance. There are three distinct endotherms (A, B and C) in this curve.

Figure 26

DTA & TGA OF EXPANDABLE POLYSTYRENE



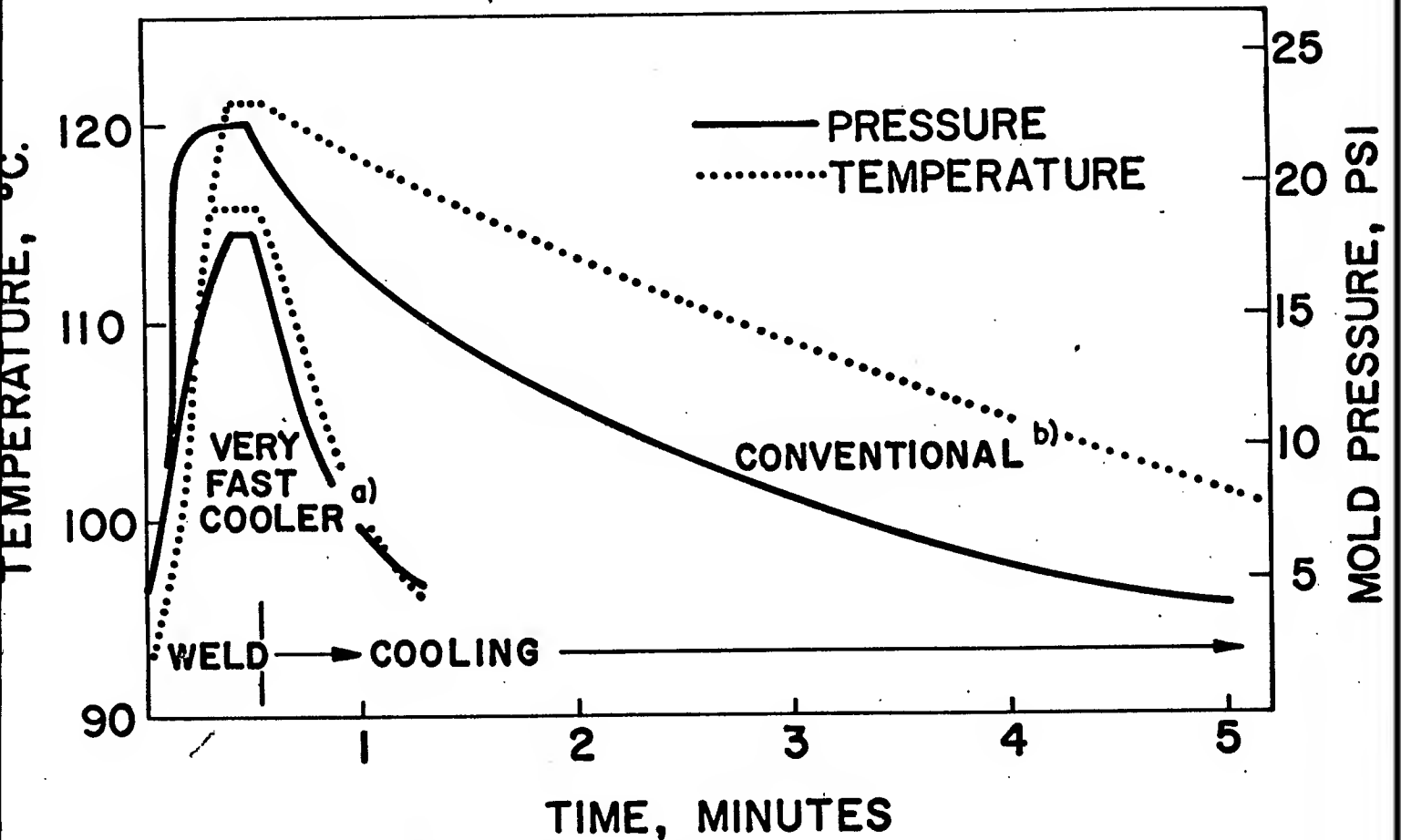
At 50°C (A) pentane starts to evaporate at a noticeable rate. It is believed that motion of some phenyl groups begins at this point (10, 11). At 85°C (B) expansion starts and the loss of pentane is accelerated. We believe B is the true glass transition point of pentane-softened polystyrene. If the pentane is removed by evaporation, a value of 98°C is obtained. The starting polymer gives a value of 100°C. The final endotherm at C occurs over a range of temperature, 115-125°C, which happens to bracket the steam-molding temperature, 119-124°C, of the foam. We think the final absorption of heat may be caused by flow of polymer when the foam collapses.

The Molding Process

The molding process was adequately described in last year's Cellular Plastics Polymer Conference by P. B. Nelson and R. H. Immel (12). We have no new information to present at this time, but our discussion would be incomplete without reviewing the main steps of the molding process, which is really a second expansion step. Steam molding is especially significant because it is the means by which expandable polystyrene beads have attained their commercial success (13). Figure 27 depicts the changes in pressure and internal temperature that occur when two different types of pre-expanded beads are molded into 4-inch-thick by 8-inch-diameter foams of 1 pcf. density in slightly vented molds. Steam at 30 psig is injected for one-half a minute through ports one-inch apart in the face plates during which the particles undergo a very rapid expansion of about 70%, fill the voids and weld together. Steam injection is ordinarily stopped when the foam exerts the desired maximum pressure against the mold. Tap water is then circulated in the steam chests until the original clamping pressure (4 psig) is reached. You will note that the cooling time

Figure 27

P-T CHANGES IN 4-IN. THICK 1 LB./FT.³ FOAMS DURING MOLDING



DYLITE[®] KFP-162^{a)} and F-40^{b)}, SINCLAIR-KOPPERS CO.

(4.5 minutes) of the conventional foam comprises the major time of the molding cycle. On the other hand, the very-fast-cooling foam requires only 3/4 minute to cool.

The mechanism of cooling of polystyrene foams has been studied in several laboratories. In Fig. 28 the data of Pogany are condensed to show the temperature 6 inches into the middle of slow- and fast-cooling foams (5). The temperature at the surface is also plotted. The slow-cooling foam exhibits the expected effect that the interior is hotter than the exterior, and it may be concluded that a substantial amount of heat is removed by conduction. However, with the fast-cooling material, the inside of the foam is actually cooler than the outside. The quick-cooling effect is believed to be caused by diffusion of pressure-generating gases (steam, air and pentane) out of the block, causing a reduction in pressure and temperature. You will recall that in Fig. 15 and 16 were electron micrographs of windows of fast- and slow-cooling foams, indicating that the windows of the fast-cooling foams have thinner areas through which diffusion of gases might occur.

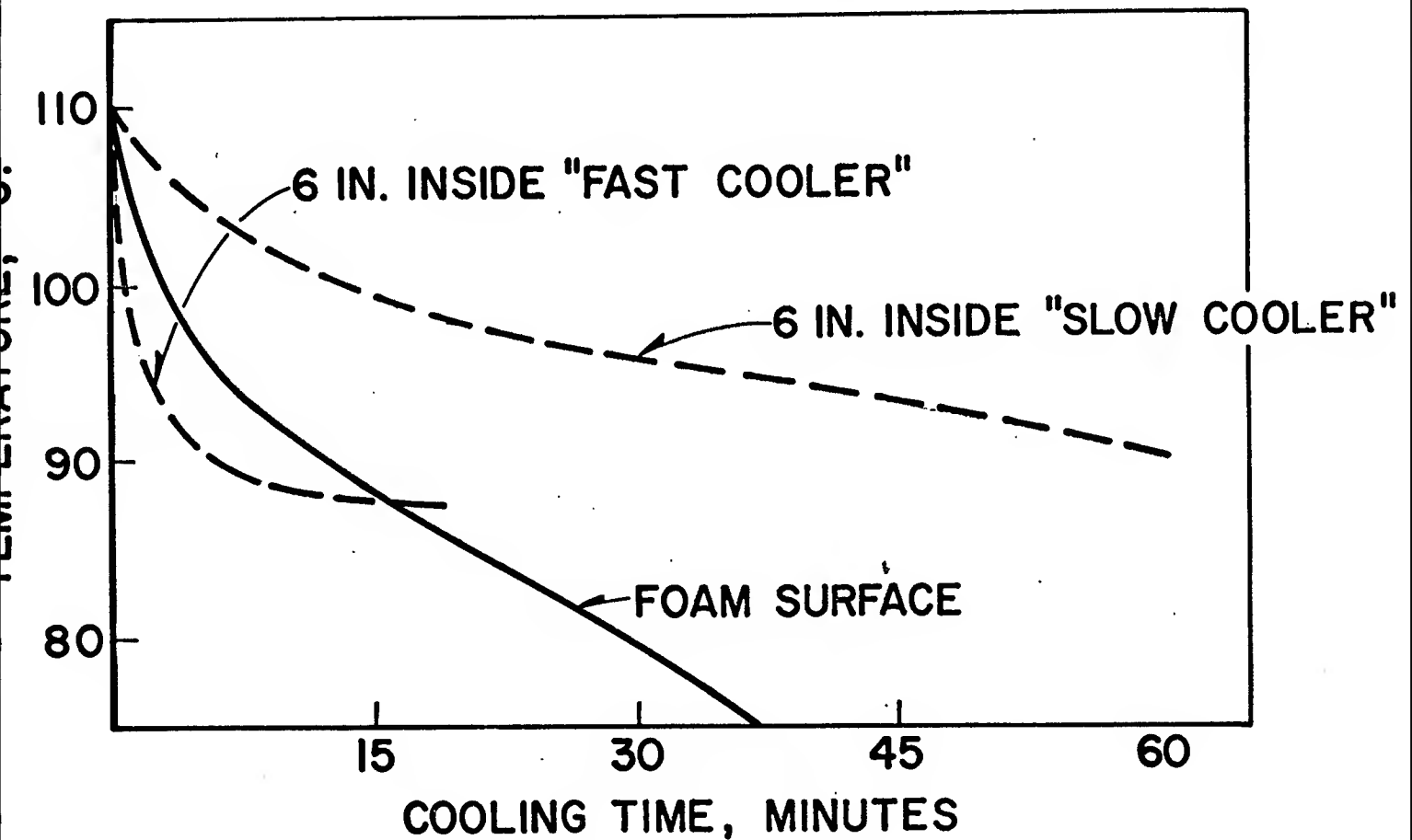
Conclusion

Methods have been developed for studying several aspects of polystyrene foam structures. These structures have been related to performance characteristics. The concept that expandable polystyrene is a dispersion of the liquid hydrocarbons fitted into cages formed by rigid chains agrees with some independent investigations on free volume. The effects of certain variables in polymeric and pentane structures have been defined in terms of shelf life and expandability. Three endotherms observed on heating expandable polystyrene were related to separate physical phenomena, as well as the expansion and molding processes.

Figure 28

TEMPERATURES OF FAST-VS. SLOW-COOLING FOAM BLOCKS

(POGANY)^{a)}



^{a)} BRITISH PLASTICS, 37, 506 (1964)

References

1. Modern Plastics, 44, 120, 121 (January, 1967).
2. Ingram, A. R., R. R. Cobbs and L. C. Couchot, "The Microscopical Examination of Molded and Extruded Polystyrene Foams," paper presented at 69th Annual Meeting of the A.S.T.M., in Symposium on Resinography of Cellular Plastics, Atlantic City, N.J., June, 1966.
3. Ingram, A. R. and H. A. Wright, Mod. Plastics, 41, 152 (November, 1963).
4. Ingram, A. R., J. Cellular Plastics, 1, 69 (1965).
5. Pogany, G. A., Brit. Plastics, 37, 506 (1964).
6. Skinner, S. J., S. Baxter and P. J. Grey, Plastics Inst. (London) Trans. J., 32(97), 180 (1964).
7. Haward, R. N., H. Breuer and G. Rehage, J. Polymer Sci., Part B, 4(6), 375 (1966).
8. Biltz, W., Raumchemie der Festen Stoffe, Voss, Leipzig, 1934.
9. Ferry, J. D., Viscoelastic Properties of Polymers, Wiley, N.Y., 1961, pp 219, 225.
10. Yamamoto, K. and Y. Wada, J. Phys. Soc. Japan, 12, 374 (1957).
11. Illers, K. H. and E. Jenckel, J. Polymer Sci., 41, 528 (1959).
12. Nelson, P. B. and R. H. Immel, "Molding of Expandable Polystyrene Foam," paper presented at Wayne State University Polymer Conference on Cellular Plastics, Detroit, Mich., 1966.
13. Buchholz, K. and F. Stastny (to Badische Anilin- & Soda-Fabrik A.G.), U.S. Patent 3,001,954 (September 26, 1961).

10214-06

ABSTRACT

Diffusion of Gases in Polymeric Foams

by

E. F. Cuddihy and J. Moacanin

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

Diffusion rates for carbon dioxide were determined on closed-cell polyurethane foams of varying densities by monitoring, for two to three weeks, the loss of weight of specimens suspended in a vacuum of 10^{-7} mm Hg. The experimental data were used to calculate diffusion coefficients for these materials, and were found to be of the order of 10^{-6} to 10^{-5} cm²/sec between 22 and 81° C.

The solution of the diffusion equation for an idealized model for a foam yielded the following expression for the diffusion coefficient:

$$D = kP_e \left(\frac{\rho_0}{\rho} \right) \left[\frac{1}{(1 - \rho/\rho_0)^{1/3}} + 1 + (1 - \rho/\rho_0)^{1/3} \right]$$

which relates the diffusion coefficient D to the foam density ρ , and to the permeation constant P_e and the density ρ_0 of the bulk polymer; k is a semi-empirical constant.

Using this equation and experimentally obtained values of D , a P_e of 5.1×10^{-9} (cc STP) mm/sec/cm²/cm Hg was calculated for the polyurethane material comprising the foam, which agrees within a factor of 2 for reported P_e constants for polyurethane.

DIFFUSION OF GASES IN POLYMERIC FOAMS*

E. F. Cuddihy and J. Moacanin

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

* This paper represents one phase of research performed by the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration, Contract NAS7-100.

INTRODUCTION

Currently, there is considerable interest in the possibility of using polymeric foams as light-weight encapsulants for electronic components on spacecrafts. Very little is known, however, on the electrical breakdown behavior in foams. In this respect an important parameter is the pressure of the blowing gas within the foam cells, in particular, in the ionization region for the gas. Therefore, a study was undertaken of the diffusion of the blowing gas from foams when placed in high vacuum. The fundamental aspects of this process are of importance to the general problem of transport properties of inhomogeneous synthetic or natural polymeric systems.

The purpose of this report is to present: (a) a relationship which was developed to relate the diffusion constant for a foam to its density and the permeation constant of the bulk polymer, (b) a description of the experimental techniques used for this study, and (c) experimental results obtained on closed cell polyurethane foams.

DIFFUSION EQUATIONS

Diffusion equations for polymeric foams were developed using as a simple, but physically reasonable model, a three-dimensional array of cubical cells having walls of uniform thickness and permeable to gases. Here, we consider only one-dimensional diffusion, although extension to the three-dimensional case is straightforward.

The general relation for the flux, J , at which a gas permeates through a membrane:

$$J = dw/dt = \frac{P_e A}{L} \Delta P \quad (1)$$

where:

w = wt. of gas

P_e = permeation constant

A = area

L = thickness of membrane

ΔP = pressure difference across the membrane

t = time

The net flux for the n -th layer of cells will be given by:

$$dw_n/dt = J_{n+1} - J_{n-1} \quad (2)$$

which upon substituting for J yields:

$$(L/P_e A) \frac{dw_n}{dt} = P_{n+1} - 2P_n + P_{n-1} \quad (3)$$

From the perfect gas law:

$$w_n = P_n VM/(RT) \quad (4)$$

which can be substituted into eq. (3) to yield the following differential equation:

$$\frac{LVM}{P_e ART} \frac{dP_n}{dt} = P_{n+1} - 2P_n + P_{n-1} \quad (5)$$

for the pressure P_n in the n-th layer of cells.

Thus for a system of N layers, one has a set of N linear homogeneous equations. For the boundary condition that the external pressure is always zero, along with the initial condition that for zero time, the pressure P_0 in all layers is uniform, the following relationship is obtained:

$$\frac{P_n(t)}{P_0} = \sum_{k=1}^N \alpha_k \left(\sin \frac{\pi n(2k-1)}{2N+1} \right) \exp \left\{ - \left[\frac{P_e ART}{LVM} \right] \left[2 - 2 \cos \frac{\pi(2k-1)}{2N+1} \right] t \right\} \quad (6)$$

For the limiting case of $N \rightarrow \infty$, the coefficients α_k 's can be readily evaluated, and the solution becomes:

$$\frac{P_n(t)}{P_0} = \frac{4}{\pi} \sum_{k=1}^{\infty} \frac{1}{(2k-1)} \sin \left(\frac{\pi(2k-1)n}{2N} \right) \exp \left\{ - \left[\frac{RTAP_e}{VML} \right] \left[\frac{\pi(2k-1)}{2N} \right]^2 t \right\} \quad (7)$$

If $N > 20$, values of α_k 's for the limiting case of $N \rightarrow \infty$ can be used without introducing a significant error. Inasmuch as for a 1 inch thick foam, N is of the order of a few hundred, eq. (7) is applicable for all cases of interest. Now, if formally we consider the gas as a diffusion process in a medium characterized by diffusion constant D, the following well-known equation is appropriate (Reference 1):

$$\frac{P_x}{P_o} = \frac{C_x}{C_o} = \frac{4}{\pi} \sum_{k=1}^{\infty} \frac{1}{(2k-1)} \sin \left(\frac{\pi x(2k-1)}{2a} \right) \exp \left\{ - \left[\frac{(2k-1)\pi}{2a} \right]^2 Dt \right\} \quad (8)$$

where:

C_x = conc. of gas

C_o = initial concentration

a = thickness of solid

x = distance in from exposed surface

D = diffusion constant

This equation is identical to eq. (8) only at the limit $N \rightarrow \infty$. But, again it will be a close enough approximation for large N . Noting that since $n/N = x/a$, the coefficients in both equations are identical and hence the arguments of the exponential for eqs. (7) and (8) must be equal, thus:

$$\frac{D}{a^2} = \frac{P_e RTA}{VMLN^2} \quad (9)$$

As V/A is the length of the side of a cell d , we substitute and rearrange Eq. (9) to get:

$$D = P_e \left(\frac{RT}{M} \right) \frac{a^2}{(NL)(Nd)} \quad (10)$$

a is the thickness of the foam, NL is the total thickness of the membranes and Nd is the total thickness of the cells; thus $a = NL + Nd$. The ratio $a^2 / \{(NL)(Nd)\}$ can be readily expressed in terms of the densities of the foam (ρ) and the bulk polymer (ρ_o). For a cube of unit dimensions, i.e., $a=1$, which contains N^3 cells, the total volume of cells is $(Nd)^3$. This volume represents the volume fraction of voids and is therefore equal to $(1 - \rho/\rho_o)$. Thus (Nd) is equal to $(1 - \rho/\rho_o)^{1/3}$ and since $(Nd) + (NL) = 1$, (NL) is equal to $1 - (1 - \rho/\rho_o)^{1/3}$. Substituting for (NL) and (Nd) in eq. 10 and factoring out ρ_o/ρ , the following expression is obtained:

$$D = (K) (P_e) \left(\frac{\rho_o}{\rho} \right) \left[\frac{1}{(1 - \rho/\rho_o)^{1/3}} + 1 + (1 - \rho/\rho_o)^{1/3} \right] \quad (11)$$

Where: ρ = density of foam
 ρ_0 = density of membrane material
 K = constant

This equation relates the diffusion constant of a polymer foam to the permeation constant and foam density. The expression

$$\left[\frac{1}{(1-\rho/\rho_0)^{1/3}} + 1 + (1-\rho/\rho_0)^{1/3} \right]$$

varies slowly between 3 and 3.05 as ρ/ρ_0 varies between 0 and 0.5. Since most polymer foams are of low density, the variation in this term can be neglected. The constant K absorbs this term and also the term (RT/M) . Thus for a given family of foams, eq. 11 predicts that the diffusion constant is inversely proportional to the foam density.

The experimental data are obtained by measuring the wt. loss, Q , from polymer foams in vacuum. The value of D is then calculated by use of the integrated form of equation (8) (Reference 1):

$$Q = Q_\infty - \frac{8Q_\infty}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{(2k-1)^2} \exp \left\{ - \left[\frac{(2k-1)\pi}{2a} \right]^2 Dt \right\} \quad (12)$$

where Q_∞ is the initial wt. of gas in the foam. For sufficiently long enough times, all the exponential terms except the first ($k=1$) can be neglected. Thus a plot of $\ln Q_\infty - Q$ versus time will eventually become linear with a slope of $\left[\frac{\pi}{2a} \right]^2 D$.

EXPERIMENTAL

To obtain wt. loss data, foams of 3" diameter and 1" deep were bonded into aluminum containers leaving the top surface exposed. The bonding agent was Eccobond 55, a room temperature curing epoxy distributed by the Emerson and Cummings Corporation.

Wt. loss data at room temp, $22 \pm 1^\circ\text{C}$, were obtained using an Ainsworth Vacuum balance unit. The balance and details of sample suspension are shown in Figs. 1 and 2.

For elevated temperatures, wt. loss was measured employing a Cahn RH Electrobalance which was situated inside a vacuum unit manufactured by the Consolidated Vacuum Corporation. The sample was heated by means of a variac-controlled 250 watt bulb. A

temperature differential of less than one degree was maintained across the sample by means of a reflecting aluminum shroud (Figs. 3 and 4).

The following polymer foams were investigated:

1. Eccosil 5000, a syntactic silicone foam of nominal sp. gr. 0.48. Prepared by mixing together hollow silicone spheres and a silicone resin.
2. Eccofoam SH, a nominal 8 lbs/ft³ polyurethane foam filled with CO₂ gas. This material is purchased already blown in 1" thick sheet stock. Actual measured density of the sample was 7.6 lbs/ft³.
3. Stycast 1090, a syntactic epoxy foam prepared by mixing together hollow glass spheres and an epoxy resin. System cures hard with a nominal sp. gr. of 0.78.
4. Eccofoam FPH/12/2H, a nominal 2 lbs/ft³ polyurethane foam filled with CO₂ gas. Material prepared prior to test by mixing a resin-catalyst system and allowing the combination to foam and cure. Density of sample was 2.1 lbs/ft³.
5. Eccofoam FPH/12/6H, a nominal 6 lbs/ft³ polyurethane foam filled with CO₂ gas. Material prepared prior to test by mixing a resin-catalyst system together and pouring into a mold which was 2" deep and 3" in diameter. Using an appropriate weight schedule, the foaming reaction would result in about half of the cured material extending above the top of the mold. Samples prepared from the top and bottom halves were respectively found to be 4.5 and 6.4 lbs/ft³.

The initial wts. of CO₂ gas (Q_{∞} , mg) in all foams were calculated using the perfect gas law.

RESULTS AND DISCUSSION

Weight loss curves for Eccosil 5000, Eccofoam SH and Stycast 1090 are shown in Fig. 5, whose outgassing rates parallel the relative order of their respective gas permeability constants (Ref. 2). Eccosil 5000 lost 180 mg of weight in 225 hours, approximately 90 mg more than the calculated CO₂ content of 90 to 100 mg (Q_{∞}). The additional wt. loss presumably arises from volatile impurities or volatile components which were not consumed in the curing reaction.

The rate of wt. loss for Stycast 1090 is extremely low as only 3.5 mg out of a possible 70 mg of gas were removed under vacuum

in approximately 130 hours. This is to be expected since the CO_2 gas is contained inside glass spheres of low permeability. In addition, the high density of this material results in the formation of very thick membranes between the glass spheres.

The rigid closed-celled polyurethane Eccofoam SH (density = 7.6 lbs/ft³) is obtained already prepared in 1 inch thick sheets. From the wt. loss data (Fig. 5) for $Q_\infty = 184$ mg, the plot of $\log(Q_\infty - Q)$ versus time was constructed as shown in Fig. 6. Using eq. (12) and the slope of the linear portion of the curve ($t > 120$ hrs), a diffusion coefficient of 2.40×10^{-6} cm²/sec at 22° C was calculated.

The family of rigid, closed-cell polyurethane foams known as Eccofoams FPH are prepared by mixing together a liquid catalyst and a liquid resin. It takes about five minutes for the system to react, foam, expand and cure. The FPH foams are asserted by the manufacturer to be capable of withstanding indefinite exposure to a temperature of 300°C, and even to higher temperatures for short periods of time. These materials are available in the density range from approximately 2 to 10 lbs/ft³.

Wt. loss curves at 22°C for three Eccofoam FPH systems of densities 2.1, 4.5 and 6.4 lbs/ft³ are shown in Fig. 7. Using these data, plots of $\log(Q_\infty - Q)$ vs. time were obtained (Fig. 8), and the diffusion coefficients were found to be 6.2×10^{-7} cm²/sec for the 2.1 lb/ft³ foam, 1.76×10^{-6} cm²/sec for the 4.5 lb/ft³ foam, and 1.24×10^{-6} cm²/sec for the 6.4 lb/ft³ foam. These values were obtained using for Q_∞ values which were calculated assuming for the initial gas pressure one atmosphere. These correspond to Q_∞ of 203 mg of CO_2 for the 2.1, 194 mg for the 4.5 and 188 mg for the 6.4 lbs/ft³ foam.

From Eq. (11), the diffusion coefficient should be inversely proportional to the density. This relationship is obeyed for the 4.5 and 6.4 lbs/ft³ foams, but not by the 2.1 lb/ft³ foam, which in fact has the lowest diffusion coefficient of the three. However, this is inconsistent with faster initial outgassing rate observed for the 2.1 lb/ft³ foam. This discrepancy can arise from an incorrectly chosen value of Q_∞ . Eq. (12) shows that D is inversely proportional to Q_∞ . Thus a higher value of D can be obtained from the $\log(Q_\infty - Q)$ plots by using a lower value of Q_∞ . Support for the use of a lower value of Q_∞ can be seen from Fig. 7 where the wt. loss curve for the 2.1 lb/ft³ foam is apparently approaching an asymptotic value of Q_∞ which is considerably less than the calculated value of Q_∞ . However, from the relationship between the diffusion coefficient density (eq. 11) along with the diffusion coefficients for the 4.5 and 6.4 lbs/ft³ foam, a value of

3.76×10^{-6} cm²/sec is predicted for the 2.1 lb/ft³ foam. Using the latter value for the diffusion coefficient, and wt. loss data, a trial and error procedure yielded a value of Q_{∞} of 148 mg. Fig. 9 is a plot comparing the $\log (Q_{\infty} - Q)$ plots for the values of Q_{∞} of 203 and 148 mg. Fig. 10 is a normalized plot of Q/Q_{∞} versus time for all three Eccofoam FPH foams and it can now be seen that the wt. loss curve for the 2.1 lb/ft³ has assumed its expected relationship in relation to the other two foams.

It should be pointed out that extrapolation to zero time of the linear portion of plots of $\log (Q_{\infty} - Q)$ vs time should intercept at a value of $\log (8Q_{\infty}/\pi^2)$ (Eq. 12). Thus, if the diffusion coefficient is independent of concentration, the diffusion equations will predict both the value of Q_{∞} and D for a given set of wt. loss vs. time data. It was found for the 6.4 lb/ft³ foam that the calculated value of Q_{∞} coincided with that obtained by back-extrapolation, justifying the use of the perfect gas law to calculate Q_{∞} .

But extrapolation of the $\log (Q_{\infty} - Q)$ plot for the 4.5 lb/ft³ foam did not yield the calculated value of $Q_{\infty} = 194$ mg. In fact, no value of Q_{∞} less than 194 mg would satisfy the equation for the given set of data. Inspection of the $\log (Q_{\infty} - Q)$ plot for this foam shows that there is greater drop in the initial portion of the curve than that observed for the 6.4 lb/ft³ foam. For the 2.1 lb/ft³ foam which also failed to satisfy the equations the drop in the initial portion of the $\log (Q_{\infty} - Q)$ curve is greater yet. This behavior is most readily attributed to a pressure dependence of the diffusion coefficient, which becomes more pronounced with decreasing foam density. If for a polymer foam the initial diffusion coefficients are higher, then the initial portion of the $\log (Q_{\infty} - Q)$ would drop more rapidly and then after a long time, the asymptotic diffusion coefficient can be obtained from the linear portion. But because of the initial larger drop, back extrapolation will yield a lower value of $\log (8Q_{\infty}/\pi^2)$, and this is observed for the 4.5 and 2.1 lb/ft³ foams.

The foregoing has shown that the initial gas contents of polymer foam of densities greater than 4.5 lbs/ft³ can be determined from the perfect gas law. Also, there seems to be little if any dependence of the diffusion coefficient on pressure for densities greater than 6.4 lbs/ft³ and thus both wt. loss and pressure distributions can be predicted employing a single diffusion equation and the diffusion equations for a homogeneous solid. Based on the 4.5 and 6.4 lb/ft³ foams, it was possible to establish the value of the constant in the equation relating the diffusion coefficient to the inverse of the density. This

equation for the Eccofoam FPH polyurethane foams is:

$$D = 7.9 \times 10^{-6} / \rho$$

where D has the units of cm^2/sec and ρ has the units of lbs/ft^3 .

The permeation constant of the bulk polyurethane polymer comprising the foam material can now be calculated from Eq. (11) using the experimentally obtained diffusion coefficients. This procedure yielded a value of P_e equal to 5.1×10^{-9} (CCSTP) $\text{mm}/\text{sec}/\text{cm}^2/\text{cmHg}$, which can be compared to a value of 12×10^{-9} reported for rubbery polyurethanes (Ref. 2). However, a lower P_e value for the rigid foam material would be expected in comparison to the equivalent rubbery material (Ref. 2).

TEMPERATURE DEPENDENCE

Outgassing rates for a $4.5 \text{ lb}/\text{ft}^3$ foam were determined at 22, 41, 61 and 81 $^{\circ}\text{C}$. The tests were conducted by first heating the samples in air to the desired temperature and then subjecting them to a vacuum. It was found, however, that the samples heated in air would lose an amount of CO_2 which increased with increasing temperature. It became a practice therefore to start recording the wt. loss in air during heating. When the desired temperature was reached and the wt. loss rate slowed significantly, vacuum was applied. The results are shown in Fig. 11, for wt. loss both in air and in vacuum with zero time taken when the vacuum was initiated.

It can be seen that there is a dramatic increase in the rate of gas removal with increasing temperature. The largest change occurs between 22 and 61 $^{\circ}\text{C}$. Above 61 $^{\circ}\text{C}$ the changes are small. It is instructive to observe that at the higher temperatures, the wt. loss asymptote appears to be the value of $Q_{\infty} = 194 \text{ mg}$ which was calculated from the perfect gas law. This further justifies the use of this value in determining the diffusion coefficients from plots of $\log (Q_{\infty} - Q)$. Also using a value of $Q_{\infty} = 194 \text{ mg}$, it is seen that this foam has lost approximately 97.5% of its gas content in 180 hours at 61 $^{\circ}\text{C}$ and higher whereas only 57% of the gas content was lost in 180 hours at 22 $^{\circ}\text{C}$.

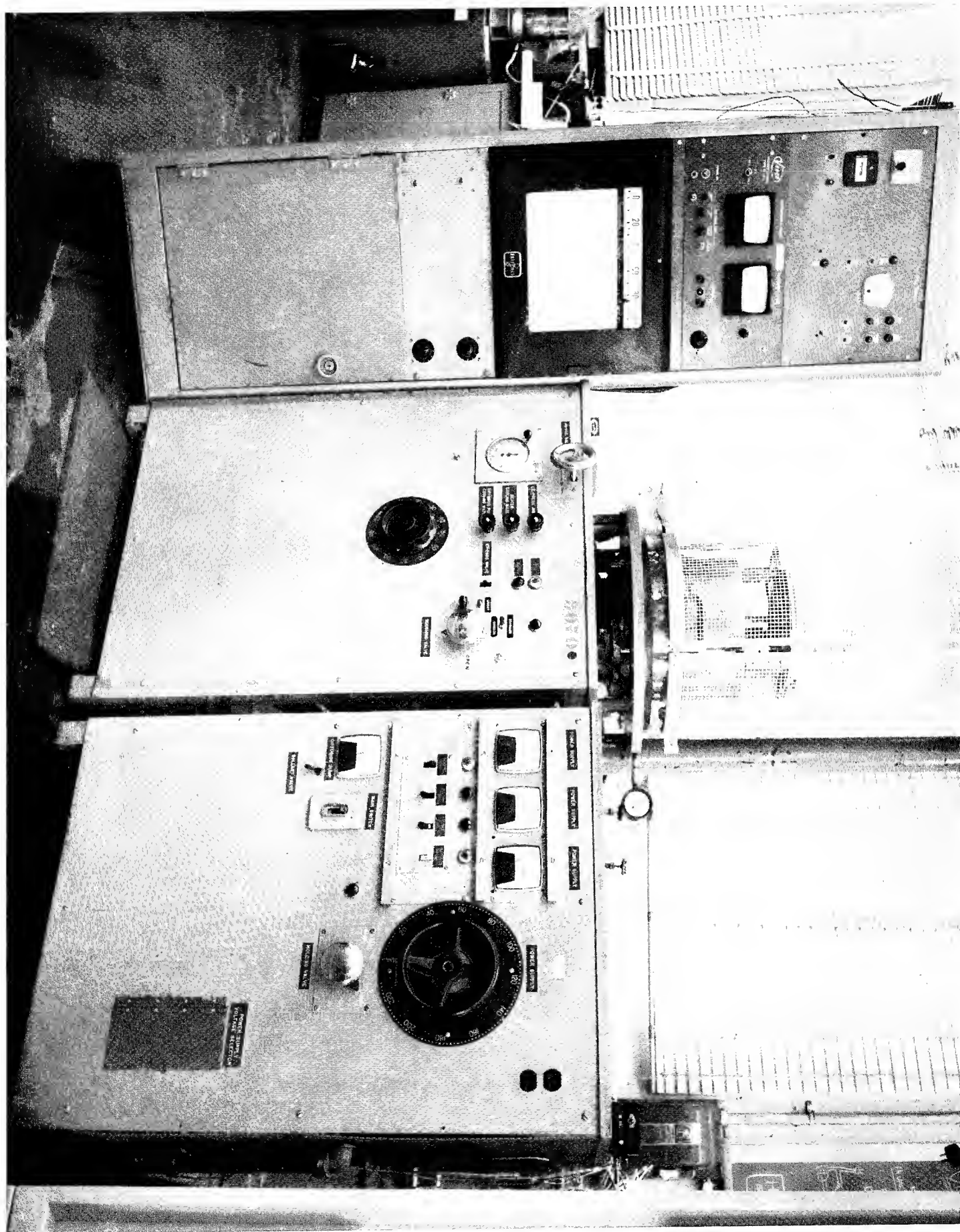
The diffusion coefficients that were obtained at the various temperatures are shown plotted in Fig. 12 as $\log D$ vs. $1/T$ in $^{\circ}\text{K}$. The general appearance of this curve is sigmoidal and indicates that the largest changes in the diffusion coefficient occurs between 22 and 81 $^{\circ}\text{C}$, above and below which there appears to be only a gradual dependence of $\log D$ on $1/T$.

REFERENCES

1. Crank, J., "The Mathematics of Diffusion," Oxford University Press, 1956.
2. Rogers, C. E., "Permeability and Chemical Resistance," Chapter 9 in Engineering Design for Plastics, sponsored by the Society of Plastics Engineers, Inc. and edited by Eric Baer, Reinhold Publishing Corporation, 1964.

FIGURE TITLES

1. Ainsworth Vacuum Balance.
2. Details of Balance and Sample Suspension.
3. Vacuum Balance Facility for Elevated Temperature Operations.
4. Details of Heating and Balance Assembly for Elevated Temperature Operations.
5. Weight Loss Curves for Three Polymer Foams at 22° C.
6. $\log (Q_{\infty} - Q)$ versus Time for Eccofoam SH at 22° C.
7. Weight Loss Curves for Eccofoam FPH Foams at 22° C.
8. $\log (Q_{\infty} - Q)$ versus Time for Eccofoam FPH Foams at 22° C.
9. $\log (Q_{\infty} - Q)$ versus Time for Eccofoam FPH/12/2H at 22° C.
10. Q/Q_{∞} versus Time for Eccofoam FPH Foams at 22° C.
11. Temperature Dependence of the Outgassing Rate for an Eccofoam FPH/12/6H Foam of Density 4.5 lbs/ft³.
12. $\log D$ versus $\frac{1}{T}$ °K for an Eccofoam FPH/12/6H Foam of Density 4.5 lbs/ft³.



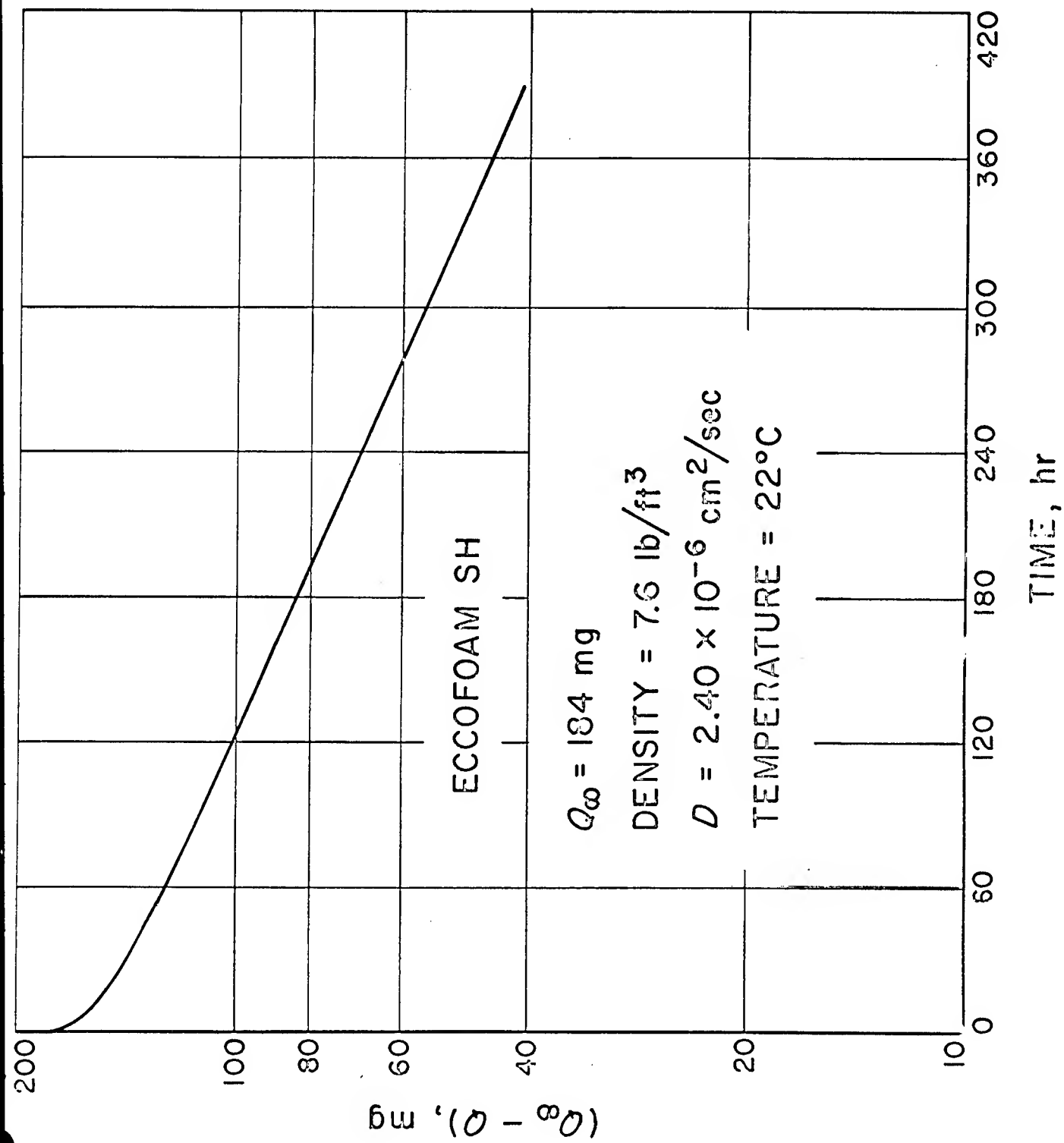


Fig. 6

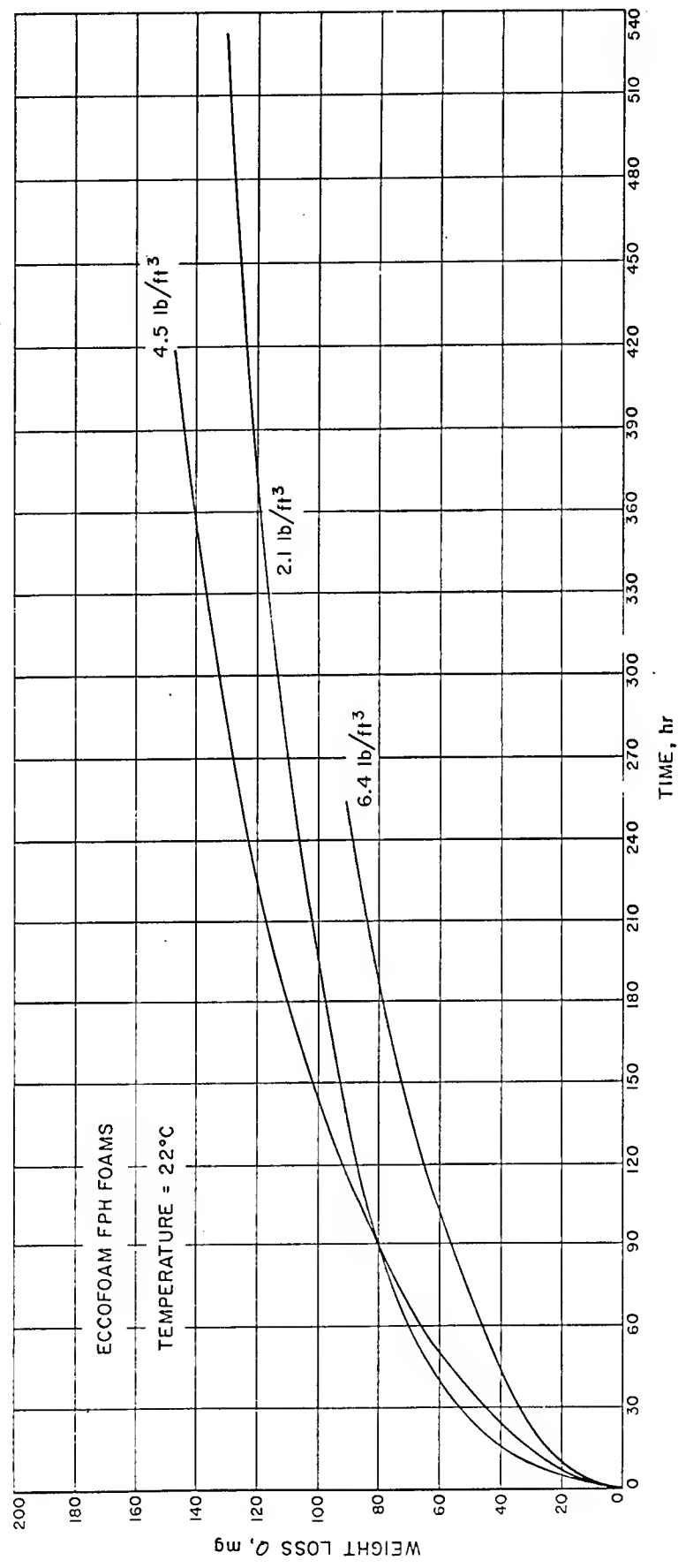


Fig. 7

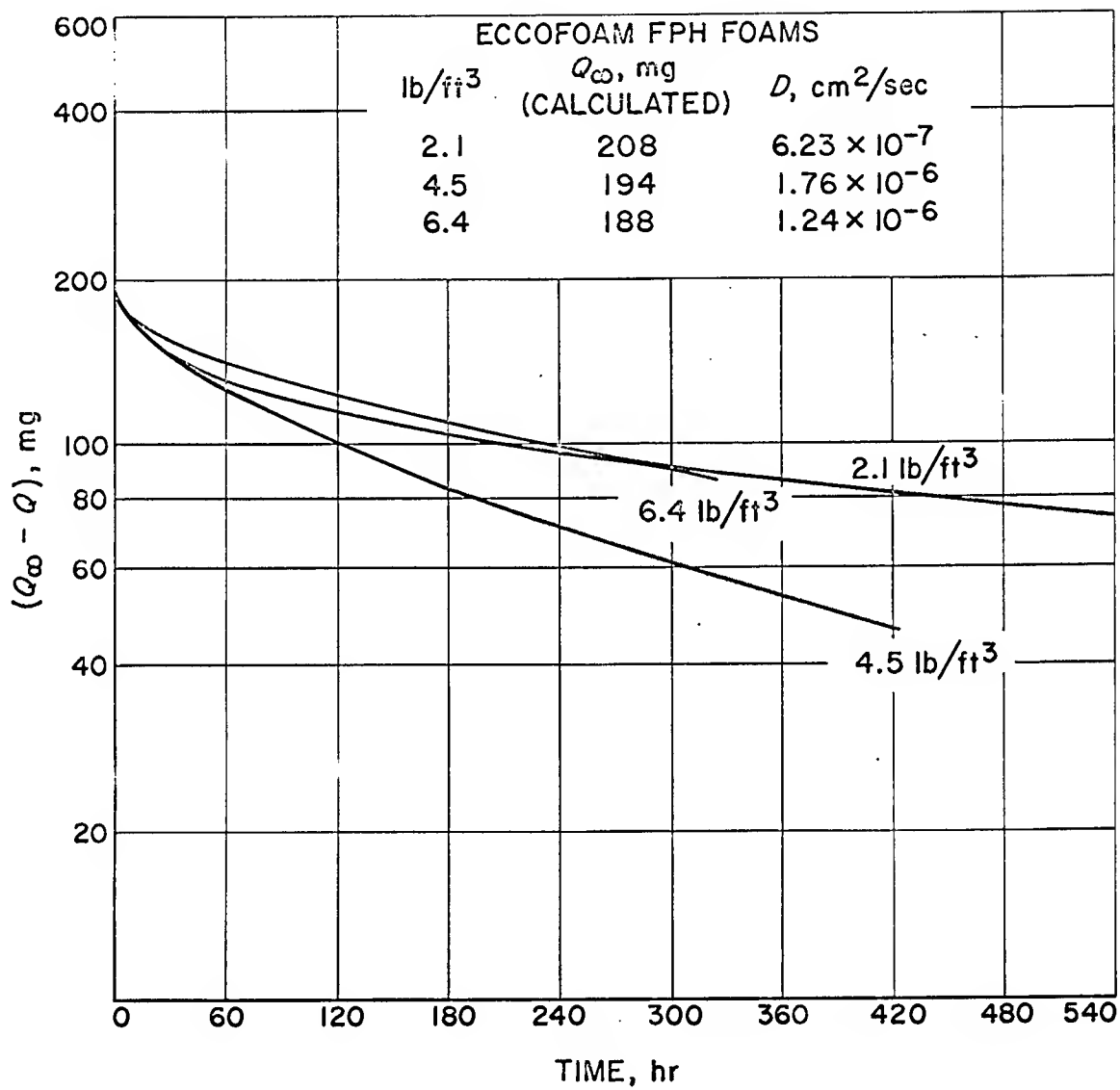


Fig. 8

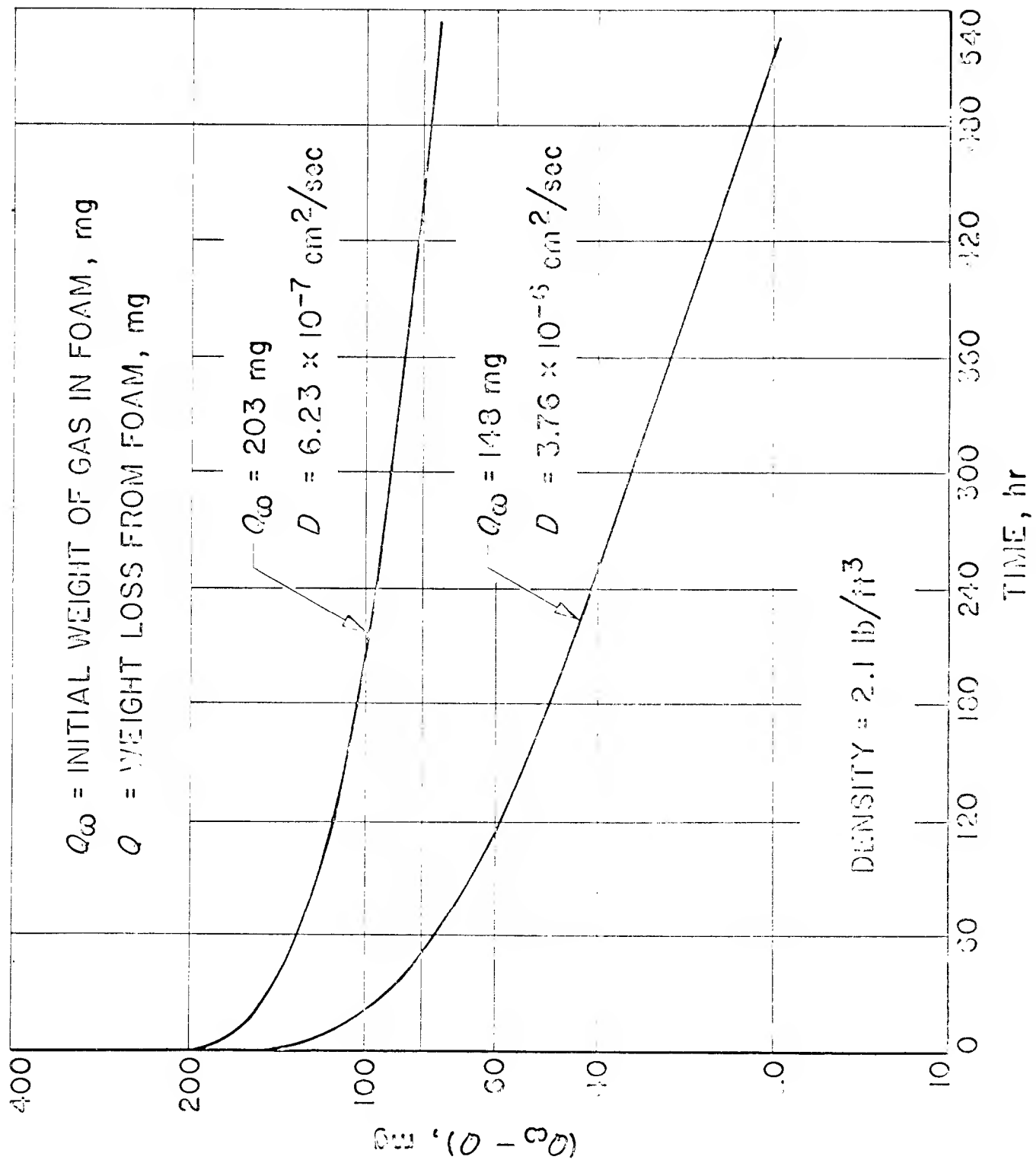


Fig. 9

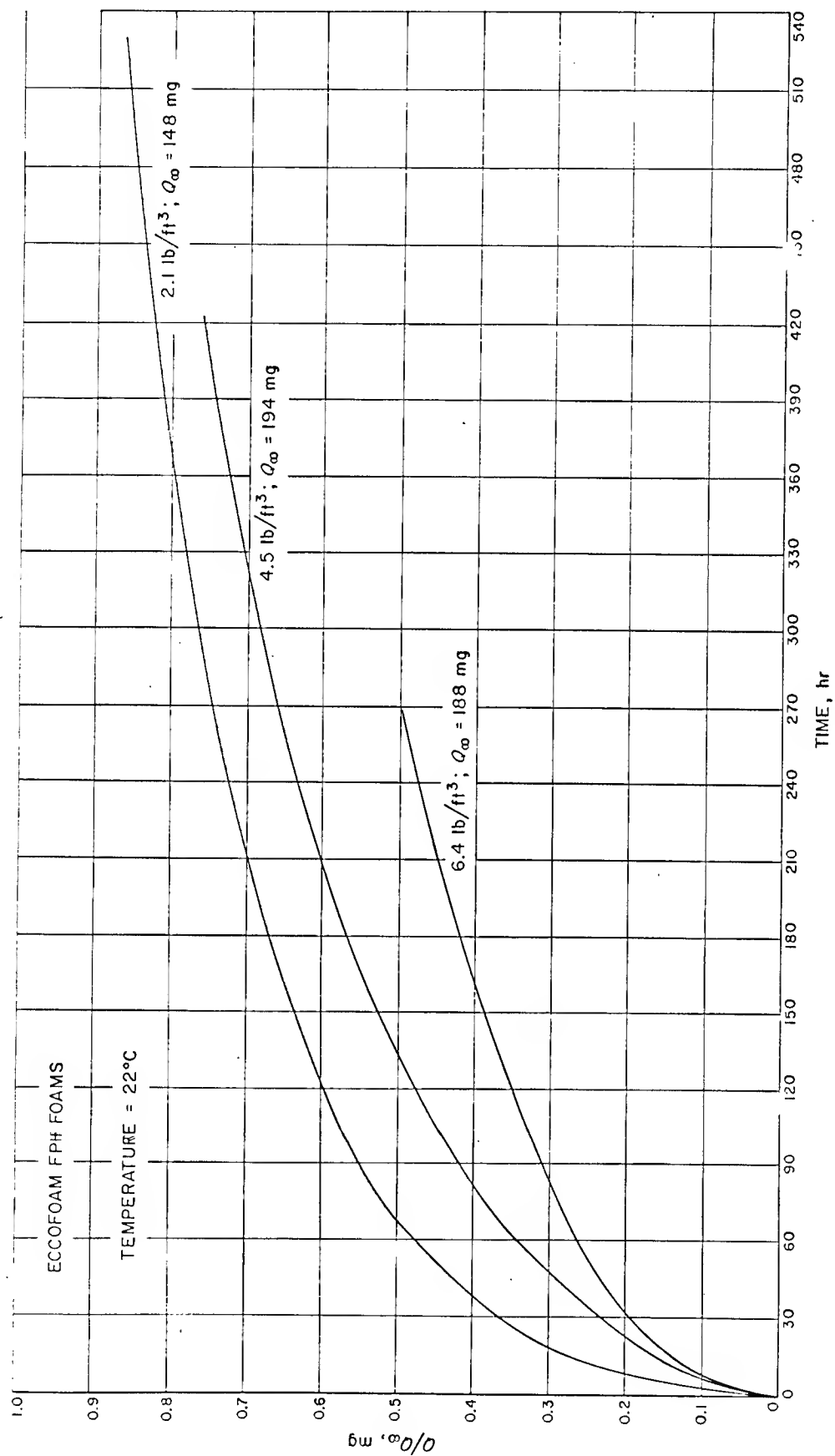


Fig. 10

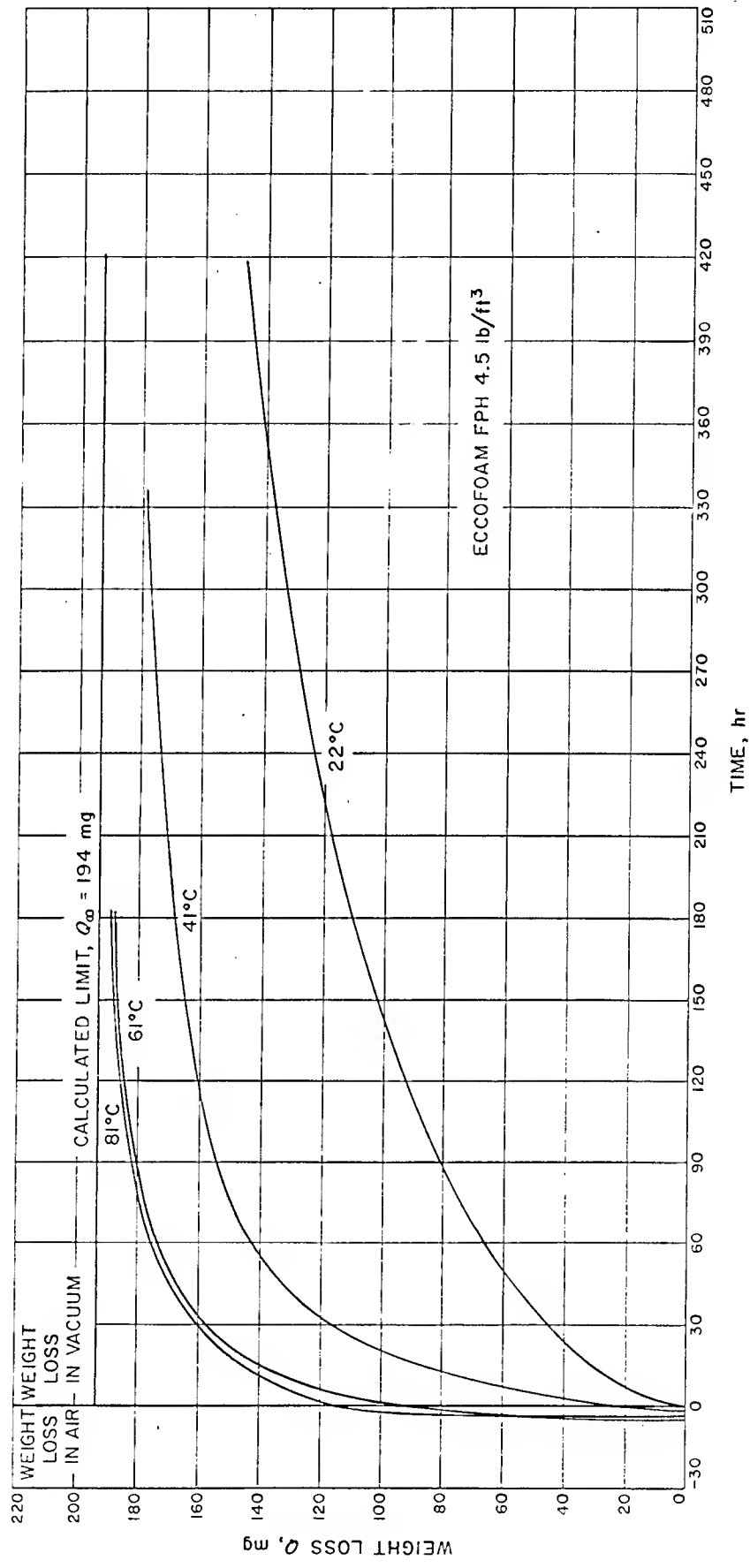


Fig. 11

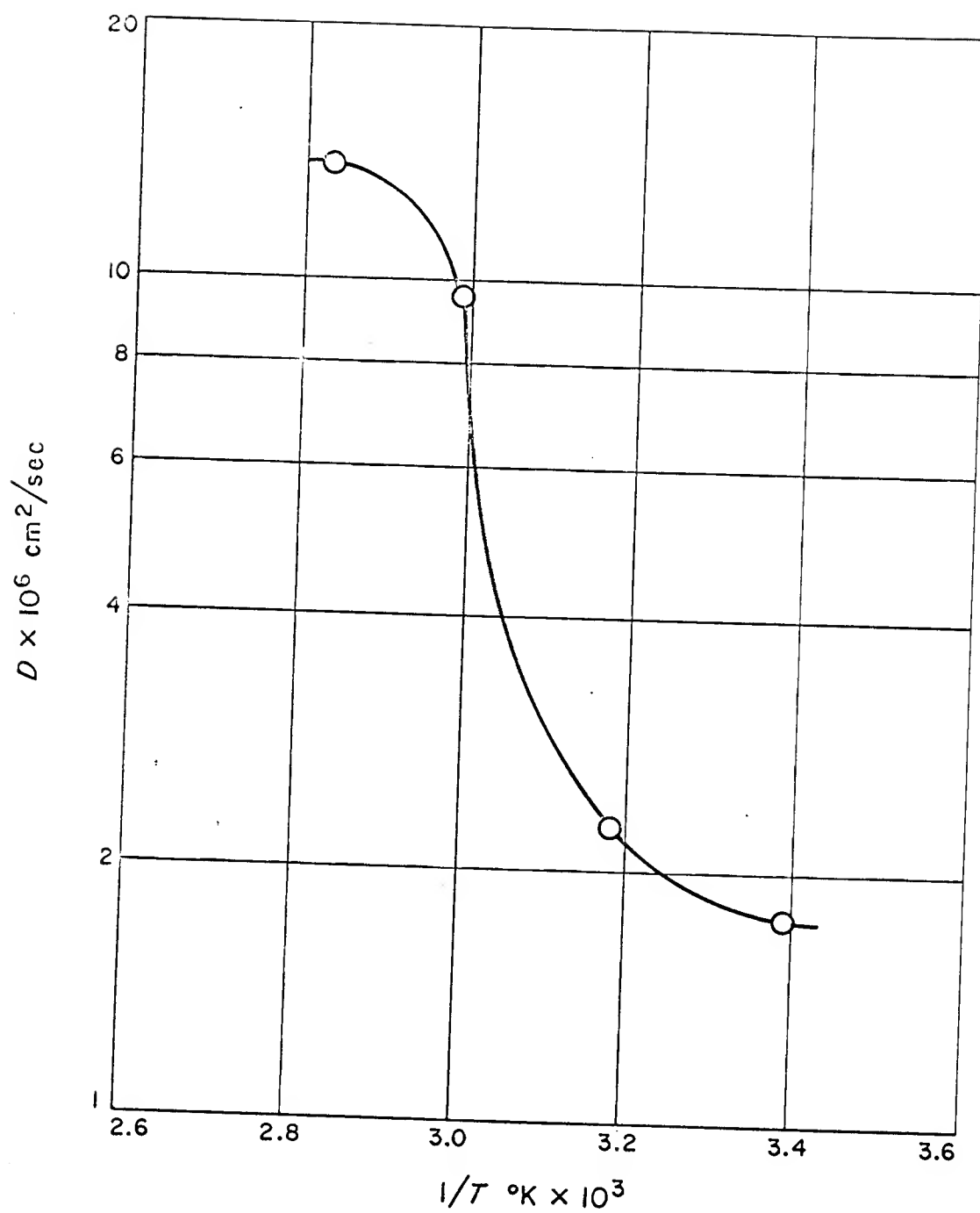


Fig. 12

10214-07

THE FLAMMABILITY CHARACTERISTICS OF CELLULAR PLASTICS

Carlos J. Hilado
Research and Development Department
Chemicals and Plastics
Union Carbide Corporation
South Charleston, West Virginia

ABSTRACT

This paper discusses cellular plastics and their flammability characteristics, describes the tests used to evaluate them, and presents some test results on materials of current significance.

Many flammability tests have been employed to describe the behavior of cellular plastics when exposed to fire. No single flammability test, perhaps no combination of a limited number of flammability tests, can predict behavior under all possible conditions of fire exposure. Each laboratory must therefore employ a system of flammability tests that satisfies both its purposes and its budget.

Different flammability tests will often give apparently conflicting results. These seeming discrepancies are actually comparisons which, related to fundamental knowledge of the mechanisms of combustion and flame extinguishment, can increase understanding of the flammability characteristics of cellular plastics and accelerate improvement of these promising materials.

THE FLAMMABILITY CHARACTERISTICS OF CELLULAR PLASTICS

Carlos J. Hilado
Research and Development Department
Chemicals and Plastics
Union Carbide Corporation
South Charleston, West Virginia

INTRODUCTION

Cellular plastics have received wide acceptance in many applications because of the advantages they offer as thermal insulation, cushioning, packaging, and flotation. Because many of these applications involve fire hazard in varying degrees, the flammability characteristics of these materials are often the factors limiting their greater use.

Many flammability tests have been employed to describe the behavior of cellular plastics when exposed to fire. Because no single flammability test, perhaps no combination of a limited number of flammability tests, can predict behavior under all possible conditions of fire exposure, the results of flammability tests must be evaluated in the context of the tests if flammability characteristics are to be properly understood.

This paper discusses cellular plastics and their flammability characteristics, describes the tests used to evaluate them, and presents the results of some of these tests on materials of current significance.

CELLULAR PLASTIC MATERIALS

A cellular plastic consists of a continuous solid phase enclosing a gas phase that is either essentially discontinuous (closed-cell) or essentially continuous (open-cell), the combination distributed uniformly enough in space to be treated as a homogeneous material. The rigidity of the polymer largely determines the rigidity of the cellular plastic.

Cellular cellulose acetate is a rigid closed-cell foam. Cellular epoxy is rigid, and may be either closed-cell or open-cell. Cellular phenolic is a rigid, largely closed-cell foam. Cellular polyethylene is closed-cell and ranges from rigid to flexible. Cellular silicone ranges from rigid to flexible, the rigid foams tending to be largely closed-cell and the flexible foams largely open-cell. Cellular urea-formaldehyde is rigid, and may be either closed-cell or open-cell. Cellular vinyl ranges from rigid to flexible, and may be either closed-cell or open-cell. Cellular polystyrene is a rigid closed-cell foam. Cellular polyurethane ranges from rigid to flexible, the rigid foams being usually closed-cell and the flexible foams open-cell.

It should be understood at this point that these cellular plastics are organic materials and will decompose if the temperature is high enough; at a high enough temperature and in the presence of sufficient oxygen, either these materials or their decomposition products will burn. Combustibility or noncombustibility is therefore a matter only of degree when these materials are involved.

The inherent flammability of the cellular plastic is almost entirely a function of the chemical composition of the solid polymer. Variations in the chemical composition of the gas phase, such as the presence of trichlorofluoromethane in most rigid polyurethane foams, have relatively little effect on flammability and are important only when the material is borderline by some flammability test. Reducing the flammability of the polymer is a highly sophisticated aspect of the science and art of formulation.

The physical structure of the cellular plastic can be of considerable importance under certain conditions of fire exposure. Closed-cell content, cell size, and polymer distribution between struts and membranes together determine the disposition in space of the multitude of microscopic "fire walls" and their supporting framework, the fire resistance

of each tiny member, the surface-to-volume and surface-to-mass ratios of the combustible material, and in certain cases the manner of decomposition and combustion. Open-cell materials are considerably more prone to internal flame spread than closed-cell materials of the same polymers, largely because of the absence of "fire walls" and the resulting "chimney effect". Foam struts substantial enough to leave a strong char skeleton tend to inhibit further flame penetration by restricting gas flow and stifling the fire with its own combustion products; complete disintegration of the foam struts results in a continual exposure of fresh surfaces to combustion.

FLAMMABILITY CHARACTERISTICS

A cellular plastic burns only when certain conditions exist. First, a unit mass at a surface exposed to oxygen must be heated to the point of ignition, or heated to the point of decomposition and at least one of the decomposition products heated to the point of ignition. The latter holds true in most cases, with ignition starting in the volatiles evolved from the pyrolysis of the material (15); this mechanism is observed in rigid polyurethane foams (25).

Second, the heat generated by the combustion of this unit mass, decreased by heat lost to noncombustible surroundings and increased by heat supplied from external sources such as an adjacent fire, must be sufficient to bring the temperature of an adjacent unit mass to its ignition point. This quantity of heat is analogous to the critical ignition energy required for the original ignition (41), and, in the case of volatiles evolution and ignition, is the energy required to heat the unit mass to the point of pyrolysis, effect pyrolysis, and heat the volatiles to the point of ignition.

Third, the heat generated by combustion of the adjacent unit mass, again adjusted for heat to and from the surroundings, must be equal to or greater than the net heat supplied by the original unit mass. If the net heat supplied by each succeeding unit mass is significantly less than the net heat from that immediately preceding, flame propagation eventually terminates.

The importance of the surroundings deserves particular emphasis, since the nature of the surroundings is the factor that characterizes and differentiates flammability tests. Because cellular plastics provide considerably less mass, and hence considerably less heat of combustion, per unit volume than

solid plastics, heat to and from the surroundings has an appreciably greater effect on net heat. An external fire source that provides a significant increase in net heat generally results in a more severe flammability test. A test chamber that confines or returns the heat of combustion to the material increases the severity of the test.

The most important flammability characteristics of cellular plastics are the following:

1. ease of ignition
2. flame spread
3. fire endurance
4. fuel contribution
5. smoke density
6. products of pyrolysis and combustion

Ease of ignition may be defined as the facility with which the cellular plastic or its pyrolysis products can be ignited under given conditions of temperature and oxygen concentration. This characteristic provides a measure of fire hazard in that a material which has an ignition temperature significantly higher than another would be less likely to contribute to a conflagration, all other factors being the same in both cases. For example, if a fire wall could be relied upon to keep the temperature on the side away from the fire below 700°F. for

a stated period of time, a material that ignited at 500°F. would be a potential hazard and a material that ignited at 900°F. would not. Some measures of ease of ignition are auto-ignition temperature, ignition sensitivity, and critical oxygen index.

Flame spread may be defined as the rate of travel of a flame front under given conditions of burning. This characteristic provides a measure of fire hazard in that surface flame spread can transmit fire to more flammable materials in the vicinity and thus enlarge a conflagration, even though the transmitting material itself contributes little fuel to the fire. Surface flammability has in recent years been the flammability characteristic that has received the most attention. Some measures of flame spread are burning rate or combustion rate, burning extent or distance of flame travel, flame spread factor, and flame height.

Fire endurance may be defined as the resistance offered by the cellular plastic to the passage of fire, normal to the exposed surface over which flame spread is measured. This characteristic provides a measure of fire hazard in that a material that will contain a fire represents more protection than one which will give way before it, all other factors being the same in both cases. For example, a cellular plastic that develops an intumescent coating or strong char upon exposure to fire would resist flame penetration much longer than one which melted away, both materials

being equal in ease of ignition, surface flame spread, and fuel contribution. Some measures of fire endurance are penetration time and resistance rating.

Fuel contribution may be defined as the heat produced by the combustion of a given weight or volume of cellular plastic. This characteristic provides a measure of fire hazard in that a material which burns with the evolution of little heat per unit quantity burned will contribute appreciably less to a conflagration than a material which generates large amounts of heat per unit quantity burned. The actual quantity of heat generated is a function of the heat developed per unit quantity burned (fuel contribution) and the quantity of material burned; the latter is a function of the area of exposed surface burned (flame spread) and the extent to which fire has penetrated into the material (fire endurance). Some measures of fuel contribution are heat evolution factor and fuel contribution index.

Smoke density may be defined as the degree of light or sight obscuration produced by the smoke from the burning material under given conditions of combustion. This characteristic provides a measure of fire hazard in that an occupant has a better chance of escaping from a burning structure if he can see the exit, and a fireman has a better chance of putting out the fire if he can see where it is.

The products of pyrolysis and combustion of cellular plastics are usually solid carbonaceous char or residue, volatile gases, and entrained solid particles (smoke). A liquid phase can result if melting occurs to an appreciable extent before charring takes place, and ignition of a liquid increases the flame spread hazard. Complete disintegration of the foam can be a significant hazard if it is relied upon for structural strength. The toxicity of the combustion gases can be a serious hazard (10).

TYPES OF FLAMMABILITY TESTS

Flammability tests are by definition tests intended to evaluate the flammability characteristics of a material. Of the six most important flammability characteristics listed, flame spread has received the greatest attention in recent years. Ease of ignition, fire endurance, and fuel contribution have received substantial attention. Smoke density, and the products of pyrolysis and combustion, are only now becoming of widespread interest. Because the study of pyrolysis and combustion products lies more in the realm of analytical chemistry rather than physical testing, it is probable that flammability tests will continue to evaluate only the other five characteristics.

Flammability tests have been extensively compared and classified on various bases (9,14,42). In this paper they will be classified on the basis of combustion factors. The basic elements of a flammability test are the specimen, the heat source, and the surroundings. All flammability tests can be classified according to these elements.

Flammability tests can be classified according to specimen size. Samples for test can generally be prepared with dimensions up to 12 inches on a laboratory scale. Samples with dimensions greater than 48 inches present problems in both preparation and handling, and the space requirements of physical facilities are substantial. Tests will therefore be classified as small-scale if the greatest specimen dimension does not exceed 12 inches; medium-scale if the greatest specimen dimension is between 12 and 48 inches; and large-scale if the greatest specimen dimension exceeds 48 inches.

Small-scale tests tend to have only a small amount of material available, and hence relatively little heat contribution from the cellular plastic. A specimen for ASTM D 1692 comprises only 6 cubic inches, compared to 6000 cubic inches when an inch-thick specimen is tested by ASTM E 84. The large-scale tests thus relate more closely to actual fire conditions.

The classification of flammability tests according to the position of the exposed surface is important, since it determines how rapidly combustion products are removed and replaced with combustion air, and how much heat transfer by convection assists in preheating the material to the ignition point. Classification will be arbitrarily based on the angle formed by the exposed surface with the horizontal. If a material burning on its upper surface is assigned the 0° position, as in ASTM D 1692, then a burning vertical surface is in the 90° position if the flame front travels upward, as in ASTM D 568; a burning lower surface at a 45° angle is in the 135° position, as in ASTM C 209; a burning horizontal lower surface is in the 180° position, as in ASTM E 84; and a burning lower surface inclined such that the flame travels downward 30° from the vertical is in the 240° position, as in ASTM E 162. Where the flame front travels directly downward, the surface is in the 270° position. This classification is illustrated in Figure 1.

The closer together in surface position that two flammability tests are, the greater the probability of establishing a satisfactory correlation between their results. Thus, most of the tests intended to predict surface flame spread by the ASTM E 84 tunnel test have a range of surface positions from

150° (the 30-30 tunnel) to 240° (the ASTM E 162 radiant panel), bracketing the 180° position in ASTM E 84. In contrast, the ASTM D 1692 test (0° surface position) appears the least likely to correlate with ASTM E 84.

Because the hot combustion gases will travel in the 90° direction if unrestrained, surface positions between 0° and 180° will have combustion gas flow concurrent with the direction of flame front travel, while surface positions between 180° and 360° will have combustion gas flow countercurrent to the direction of flame front travel. In the former case, the hot gas from each unit mass helps to heat the adjacent unit mass to the ignition point; in the latter case, the incoming combustion air needed by each unit mass cools the adjacent unit mass.

Because of the same upward tendency of the hot combustion gas, surface positions between 90° and 270° will have the pyrolysis and combustion products staying close to the surface, while surface positions between 270° and 360°, and between 0° and 90°, will have the pyrolysis and combustion products moving away from the surface. In the former case, the combustion products linger to smother the fire but the pyrolysis products linger to feed it; in the latter case, much of the combustion tends to take place away from the specimen surface.

A comparison of the available flammability tests from the viewpoint of surface position leads to the observation that almost all of them form a continuous spectrum from 90° to 240°. ASTM D 635 and D 1692 and similar tests in the 0° surface position would appear to have little prospect of correlating with their fellows.

The heat source can be such that, in relation to the heat of combustion of the unit mass, it contributes essentially nothing toward bringing the adjacent unit mass to the ignition point, as in ASTM D 1692. On the other hand, it can be substantial enough to overwhelm the resistance of most cellular plastics, as in many large-scale tests. The amount of external heat will therefore be arbitrarily classified as low, moderate, or severe.

The surroundings have an appreciable effect on the net heat available for bringing successive unit masses to the ignition point. If the geometry of the test enclosure is such that the hot combustion gases are confined and radiant heat energy is reflected or concentrated, energy feedback tends to be large and energy dissipation small. If both hot gases and radiant

heat are free to escape, then feedback tends to be small and dissipation large. The proximity of materials with large heat capacities increases dissipation unless they are preheated or insulated. At this stage, the tests will be arbitrarily classified as either high-feedback or low-feedback.

Most of the flammability tests which may be applied to cellular plastics are reviewed in the following sections. Almost all were originally designed for solid materials, some specifically for solid plastics.

SMALL AND MEDIUM SCALE TESTS

Some flammability tests employ specimens with such small dimensions that a measure of flame spread can not be obtained. They do, however, provide excellent measures of other flammability characteristics.

The ASTM D 1929 test (1) is based on the classic method and apparatus developed by Setchkin (45) and measures the self-ignition and flash-ignition temperatures of plastics. The self-ignition temperature is the lowest temperature of supplied air, under optimum conditions of air flow, at which

a reaction of the material, or its decomposition products, begins and is self-accelerated to the state of combustion. The flash-ignition temperature is that temperature at which the material yields combustible gases ignitable by a flame. A specimen weight of 3 ± 0.5 grams is required. By this test method, the flash- and self-ignition temperatures of rigid polyether urethane foam were reported to be 590°F. and 780°F., respectively; the respective figures were 680°F. and 925°F. for polystyrene, 735°F. and 850°F. for polyvinyl chloride, and 645°F. and 660°F. for polyethylene (36).

The ASTM E 136 test (1) uses essentially the same apparatus to determine noncombustibility by placing a specimen 1.5 inches by 1.5 inches by 2 inches in an air stream maintained at $1382 \pm 10^\circ\text{F}$.

A Bureau of Mines explosibility test measures ignition sensitivity and explosion severity (28). The ignition temperatures reported for rigid polyurethane foams were 390°C. to 550°C.

The General Electric test for critical oxygen index (17,18) measures the limiting concentration of oxygen which just permits steady burning down of polymer rods like candles in a gently rising atmosphere. Critical oxygen indices of 0.174

to 0.175 were reported for polyethylene, 0.181 to 0.183 for polystyrene, and 0.47 for polyvinyl chloride.

The Rohm & Haas XP2 smoke density test (39) measures the rate of smoke generation and its visibility-obscuring effects. Specimens 1 inch by 1 inch by 1/4 inch are required. The heat source is a propane-air flame from a Bernz-O-Matic TX-1 pencil-tip burner supplied with propane under 40 psi pressure, applied at a 45° angle, for a maximum of 4 minutes. This test gives smoke production rate, total smoke produced, and maximum smoke density. A Wayne State University modification (13) employs foam specimens 2 inches by 2 inches by 2 inches and a 60-second flame application time; propane pressure is 50 psi, giving a 6-inch flame with a 2-inch inner cone.

The ASTM D 1692 test (1) is perhaps the most widely known small-scale test applied to cellular plastics. It evaluates the flammability of a horizontal bar ignited at one end by a burner flame. Specimens 6 inches by 2 inches by 1/2 inch are required. The specimen is supported on a horizontal hardware-cloth support with the 1/2-inch dimension vertical. One end is ignited for 60 seconds by a 1-1/2-inch high blue flame from a 3/8-inch diameter bunsen or tirrill burner fitted with

a 1-7/8-inch wide wing top, the support being 1/2 inch above the top of the burner wing top. The extinguishment time, burning rate, and burning extent are reported, based on travel of the flame front along the upper surface of the specimen. This test is characterized as small-scale, with 0° surface position, low heat, and low feedback.

With various modifications, this test is also known as Underwriters Laboratories UL-94 (50) and Monsanto Rideal Laboratories 117/2 (7). Because of its simplicity, and low time and material requirements, it has been extensively used in formulation studies (2,9,33,38,46), and its widespread use has led to detailed investigation (25).

The ASTM D 635 test (1) evaluates the flammability of a horizontal bar ignited at one end by a burner flame. Specimens 5 inches by 1/2 inch by the supplied thickness are required. The specimen is held with the 5-inch dimension horizontal and the 1/2-inch dimension inclined at a 45° angle. One end is ignited for 30-second periods by a 1-inch-high flame from a 3/8-inch diameter bunsen burner, the tip of the flame contacting the end of the specimen. The number of ignitions, length burned, and burning rate are reported. This test is considered small-scale, with 0° surface position, low heat, and low feedback. Method 2021 of Federal Test Method Standard 406 (51) is essentially the same as ASTM D 635.

The Globar test evaluates the flammability of materials brought into contact with a surface at bright red heat. As ASTM D 757 (1), it is applied to materials found to be self-extinguishing by ASTM D 635. Specimens 5 inches by 1/2 inch by 1/8 inch are required. Each specimen is held with the 5-inch dimension horizontal and the 1/2-inch dimension vertical, and one end is placed in contact with a Globar element maintained at $950 \pm 50^{\circ}\text{C}$. ($1742 \pm 90^{\circ}\text{F}$.) by electrical input of 350 ± 20 watts, for 3 minutes. The burning rate in inches per minute is reported. This test is considered small scale, with 0° surface position, low heat, and low feedback.

A different approach is used by the National Aniline CF-TM-11 test (34), in which the specimen measuring 8 by 2-1/2 inches by 1/4 inch is held vertically and the bottom placed in contact with a Globar element, the temperature of which is raised in 25°F . increments until ignition occurs. The test provides ignition temperature, burning rate, propagation time, and extinguishment time. It is considered small scale, with 90° surface position, low heat, and low feedback.

The ASTM D 568 test (1) evaluates the flammability of a vertical bar ignited at the bottom end by a burner flame. Specimens 18 inches by 1 inch by the supplied thickness are

required. The specimen is held vertically and the bottom end ignited by a 15-second application of a 1-inch flame from a bunsen burner. Burning rate is reported. This test is considered medium scale, with 90° surface position, low heat, and low feedback. Method 2022 of Federal Test Method Standard 406 (51) is the same as ASTM D 568 except that ignition is accomplished by either a pyroxylin plastic fusee or a benzene drop.

Another vertical test is the Hooker HLT-15 test (27) which requires specimens 8 inches by 1/2 inch by 1/8 inch. The vertical specimen is ignited by successive applications of a 5-inch high flame from a 7/16 inch tirrill burner, the tip of the 1-1/2 inch inner cone touching the bottom of the specimen. Ratings based on the predetermined pattern of 5 ignitions are reported. This test is considered small-scale, with 90° surface position, moderate heat, and low feedback.

Underwriters Laboratories (50) list a similar test using a 3/4-inch-high blue flame from a 3/8-inch diameter tirrill burner for two successive 10-second ignitions. Bell Telephone Laboratories (30) employ a modification, substituting a microburner using natural gas which develops a flame temperature of 900°C, and a single 30-second ignition.

The Vertical Bar test (1) requires a specimen 18 inches by 2 inches by 2 inches. The bottom end is ignited for 60 seconds by a 1-1/2 inch high blue flame from a 3/8-inch diameter bunsen burner fitted with a 1-7/8-inch wide wing top, the burner wing top being 1/2 inch under the bottom of the specimen. Extinguishment time, flame height, weight losses, and char fraction are reported. This test is considered medium scale, with 90° surface position, low heat, and low feedback. Because the upper half of a highly flame retardant specimen is not affected, the Union Carbide procedure provides for 9-inch specimens to permit the use of this test on smaller samples.

The Butler chimney test (29) modifies the vertical specimen approach by enclosing a 10 inch by 3/4 inch by 3/4 inch specimen in a vertical steel chimney with a wire-reinforced glass front to increase energy feedback. The bottom end is ignited for 10 seconds with a bunsen burner flame with a 1 to 1-1/4 inch high blue inner cone, the tip of which is maintained at $1660 \pm 10^{\circ}\text{F}$. Extinguishment time and weight loss are reported. This test is considered small scale, with 90° surface position, low heat, and high feedback.

The Schlyter test (55) requires two specimens 12 inches wide and 31 inches high held in a vertical position with their faces 2 inches apart and with free access of air at bottom and sides. The fire source is either a bunsen burner with wing top delivering 37 Btu per minute or a No. 4 meker burner with special T-head delivering 291 Btu per minute, applied for 3 minutes in either case. This test is considered medium scale, with 90° surface position, low to moderate heat, and high feedback.

Method 2023 of Federal Test Method Standard 406 (51) is intended for plastics that are difficult to ignite, and requires specimens 5 inches by 0.5 inch by 0.5 inch. The specimen is supported in a vertical position surrounded by heating coils. A constant current of 55 amperes is applied to heat the specimen and continuous sparking of spark plugs ignites the escaping gases. Ignition is considered as occurring when the flame transfers from the escaping gases to the specimen surface. Ignition time, burning time, and distance of flame travel are reported. This test is considered small-scale, with 270° surface position, low heat, and low feedback.

The ASTM C 209 inclined panel flame test (1) requires a specimen 12 inches by 12 inches by the supplied thickness. The specimen is supported at a 45° angle and ignited at a point 3 inches from its lower horizontal edge and midway between the inclined

edges. The flame source is a flat-bottomed cup $5/8$ inch in internal diameter, $9/32$ inch deep, and $1/32$ inch thick, containing 1 ml of absolute ethyl alcohol, under the specimen. The elliptical char area is measured. This test is considered small-scale, with 135° surface position, low heat, and low feedback.

Monsanto Rideal Laboratories Method 118/2 (7) uses a similar approach. A foam specimen 6 inches by 6 inches by 2 inches thick is supported at a 45° angle so that the bottom edge of the lower face is $3/4$ inch vertically above the center of the base of the cup; the cup is the same as that described in ASTM C 209, except that it is preheated by burning 0.3 ml of absolute alcohol without the specimen in position $2-1/2 \pm 1/4$ minutes before the specimen is ignited with 0.3 ml of absolute alcohol. This test is considered small scale, with 135° surface position, low heat, and low feedback.

The ASTM E 162 radiant panel test (1) employs a radiant heat source consisting of a 12 by 18 inch vertically mounted porous refractory panel maintained at $1238 \pm 7^\circ\text{F}$ ($670 \pm 4^\circ\text{C.}$). A specimen 18 inches by 6 inches is supported in front of it with the 18-inch dimension inclined 30° from the vertical. A pilot burner ignites the top of the specimen, $4-3/4$ inches away from

the radiant panel, so that the flame front progresses downward, along the underside exposed to the radiant panel. Stack thermocouples are used to record the temperature rise which is considered a measure of heat evolution. A sample of smoke deposit is collected for optical density measurements. The test method gives flame spread factor, heat evolution factor, flame spread index, and smoke deposit. This method is considered medium scale, with 240° surface position, moderate heat, and low feedback. Operating stack thermocouple temperature was not specified in the 1960 tentative method, but was specified as $401 \pm 45^{\circ}\text{F}$. ($205 \pm 25^{\circ}\text{C}$.) in the 1962 revision. In the Union Carbide procedure, stack temperature is maintained at $400 \pm 10^{\circ}\text{F}$.

This method, also known as Interim Federal Standard 00136a (51), has been extensively studied (23,24,40,41), and is perhaps the best characterized of the medium-scale tests.

Several flammability tests employ the inclined-tunnel principle, in which the heat source is at the lower end and flame progresses upward along the bottom surface which forms the roof of the tunnel. All are considered medium scale, with moderate heat and high feedback.

The Monsanto Two-Foot Flame Tunnel (53) employs a specimen 24 inches by 4 inches inclined 28° from the horizontal (152°

surface position). The heat source is a Fisher 3-900 burner supplied with a constant 3 ounces per square inch natural gas flow. The test method gives flame-spread rating, fuel contribution, afterflaming and afterglowing, intumescence and insulative value, and smoke contribution.

A similar Monsanto apparatus (8) employs a specimen 24 inches by 3-3/4 inches inclined 30° from the horizontal (150° surface position). The heat source is a Bernz-O-Matic pencil-flame burner supplied with propane at 70 psi gage pressure through an 0.008-inch diameter orifice, which gives a heat input of 54 Btu per minute and a stack gas temperature of 320°F.

The Pittsburgh Corning 30-30 Tunnel (31) employs a specimen 30 inches by 3-7/8 inches inclined 30° from the horizontal. The flame source is a Fisher 3-900 burner supplied with 2,600 cc per minute of natural gas, which gives a steady 6 inch burner flame providing about 90 Btu per minute. A flame spread rating is reported.

The Upjohn modification of the 30-30 tunnel (44) supplies the burner with 330 ml per minute of propane, which gives a flame height of 4.4 inches and a flame temperature of 1725°F.

The Bureau of Mines flame penetration test (32) employs a specimen 6 inches by 6 inches by 1 inch, and measures the time required for the 1-inch thickness to be penetrated by a propane-air flame from a vertical Bernz-O-Matic 1351-BP pencil-flame burner head with V-1107-B fuel orifice, the flame temperature being held at $2150 \pm 25^{\circ}\text{F}$. This test is considered small-scale, with 270° surface position, moderate heat, and low feedback.

The SS-A-118b test (52) employs a specimen 36 inches by 36 inches, supported in a horizontal position with a 30 inch by 30 inch area exposed, 28-3/4 inches above a burner delivering 60,000 Btu during the 40-minute test and 28,000 Btu during the 20-minute test. This test is considered medium scale, with 180° surface position, severe heat, and low feedback.

The BS 476 flame spread test (5) employs a specimen 36 inches by 9 inches, mounted vertically and perpendicular to one side of a 3 foot by 3 foot gas-fired radiant panel, so that the flame front travels 36 inches away from the radiant panel to reach the far end of the specimen. The radiant panel is adjusted so that temperatures along the specimen surface vary according to a fixed pattern from 500°C . at the panel to 130°C . at the far end. This test is considered medium scale, with 0° surface position, severe heat, and low feedback. *exposed to set up*

The Martin Sweets test (48) is a unique test intended to simulate the conditions existing when superheated combustible vapors collect in an enclosure insulated with sprayed rigid polyurethane foam. The test enclosure is essentially a 2-foot cube with two of the four sides providing access of air.

LARGE SCALE TESTS

The ASTM E 84 test (1) is perhaps the most widely accepted flammability test; it is also known as UL 723 (50) and NFPA 255 (35). It requires a specimen 25 feet long and 20 inches wide, mounted face down so as to form the roof of a 25-foot-long tunnel 17-1/2 inches wide and 12 inches high. The fire source, two gas burners 1 foot from the fire end of the sample and 7-1/2 inches below the surface of the sample, is adjusted so that a test sample of select-grade red-oak flooring would spread flame 19-1/2 feet from the end of the igniting fire in 5-1/2 minutes \pm 15 seconds. The end of the igniting fire is considered as being 4-1/2 feet from the burners, this flame length being due to an average air velocity of 240 \pm 5 feet per minute. Flame-spread classification is determined on a scale on which asbestos-cement board is zero and select-grade red-oak flooring is 100. Fuel contribution and smoke density are

determined on a similar scale. This test has a 180° surface position with severe heat and high feedback. It has been extensively investigated and is often cited as a basis for determining fire hazard (4,11,47,56).

The FPL 8-foot tunnel test (6,37), also known as ASTM E286 (1), employs a specimen 8 feet long and 14 inches wide, mounted horizontally to give a slope lengthwise of 6° , and tilted 30° across its width. It is essentially a scaled-down modification of the 25-foot tunnel. This test has a 174° surface position with severe heat and high feedback.

The FM Calorimeter test (49) employs a specimen 4-1/2 feet by 5 feet, of which an area 4 feet by 4 feet is exposed in the roof of a furnace 17-1/2 feet long, 4 feet wide, and 3-3/4 feet high. Gasoline is used to fuel the main fire exposure burners while propane is used as the evaluating fuel. After the specimen is burned using only the fire exposure burners, it is replaced with a noncombustible cover and the evaluation burners are adjusted to reproduce the flue temperature-time curve produced by the specimen. The heat added through the evaluation burners is then equal to the heat released by the specimen. This test has a 180° surface position with severe heat and high feedback.

The Atlas tunnel test (20) employs a tunnel 2 feet high, 4 feet wide, and 10 feet long, with a wire mesh screen 16 inches from the floor serving as a platform for ducts to be tested. The fire source is excelsior with 16 ounces of kerosene, allowed to burn for 5 minutes.

The standard time-temperature curve described by ASTM E 119 (1) and UL 263 (50) is widely accepted as the "standard fire curve" and features a rapid rate of rise during the first 10 minutes of the test. It is employed in large-scale tests such as ASTM E 152 (1) and UL 10 (b) (50) for door assemblies and ASTM E 163 (1) and UL 9 (50) for window assemblies. Such tests usually involve over 100 square feet of exposed surface: an Underwriters Laboratories installation uses test frames 14 feet by 18 feet (3), while the Factory Mutual "White House" test involves a structure 20 feet wide by 100 feet long (16). Testing on such a scale is beyond the scope of most laboratories, but the standard fire curve is employed on smaller scale in-house tests such as the Union Carbide test employing a vertical panel 4 feet by 4 feet (54).

Most firms contract out large-scale fire tests to organizations such as Underwriters Laboratories and Southwest Research Institute.

FLAMMABILITY TEST SYSTEMS

It is evident that no single test can predict flammability behavior under all possible conditions of fire exposure, and that economic factors would prohibit the installation and performance of all flammability tests which could be pertinent to cellular plastics. It therefore becomes necessary for each laboratory to develop and install a system of flammability tests that satisfies both its purposes and its budget.

Flammability tests can be performed with two purposes: marketing support, and research and development. Tests performed to support marketing efforts have the following objectives in mind:

- A. Product qualification and certification
- B. Quality control
- C. Technical service

Tests that meet these objectives have either general acceptance by the industry or individual acceptance by the customer. The adoption of a test method as an ASTM or Federal standard is one indication of its degree of acceptance.

Tests performed for research and development purposes have the following objectives in mind:

- A. Normal screening to compare similar materials
- B. Basic physical/chemical structure-property studies
- C. Application and design studies

Test that meet these objectives are those which provide observations of scientific value, and meaningful data with adequate precision. Because of the rapid development of cellular plastics and relatively recent improvements in their flame resistance, such tests tend to be those being presented for consideration as standards rather than those already on the books.

The flammability test system in use by Union Carbide Corporation at South Charleston for cellular plastics appeared to be the most satisfactory system for both purposes. It consists of four tests: the ASTM D 1692 small-scale test, the vertical bar test, the ASTM E 162 radiant panel test, and the Bureau of Mines flame penetration test. These tests offer the following economic advantages: none requires a specimen more than 18 inches long, or more than 15 minutes to perform; each can be performed on a routine basis and is adapted to computer calculation and tabulation (26).

For market support purposes, two of the four tests are ASTM standards and the other two are under committee consideration,

being rather widely used by the industry. For research and development purposes, two of the tests provide a measure of ease of ignition, three provide a measure of flame spread, one provides a measure of fire endurance, two provide a measure of fuel contribution, and one provides a measure of smoke density. The three tests measuring flame spread provide three surface positions: 0° , 90° , and 240° . The geometry of pyrolysis and combustion in these tests is presented in Figures 2 through 5.

COMPARISON OF FLAMMABILITY TEST RESULTS

The burning of cellular plastics is a combustion process and can be related to basic combustion theory (15). The technology of increasing their fire resistance is both a science and an art, and involves knowledge both of the fundamental mechanisms of flame extinguishment (21,22) and of the chemistry required to apply this knowledge to these materials (12,14,19,43). This paper will limit itself to showing how changes in the flammability characteristics of some current materials were manifested in the tests used to evaluate them.

The materials were rigid polyurethane foams derived from polyoxypropylene ethers and polymeric diphenylmethane type

polyisocyanates, containing organophosphorus flame retardants. To illustrate the effect of various flame retardant additives, data were selected on nine formulations to which had been added increasing concentrations of different additives. The flammability tests employed were the four tests comprising the Union Carbide flammability test system. Some of the results are shown in Figures 6 through 21.

Comparison of these figures leads one to conclude that no general trend is present in these data, and that relative performance is highly dependent on the formulation, on the additive, and most of all on the flammability test used.

The ASTM D 1692 data, for example, indicate that formulation 6 gave the lowest burning extent and formulation 7 the highest, yet formulations 6 and 7 exhibited the highest weight losses in the vertical bar test; on the basis of the vertical bar test, formulations 1 and 3 would be judged to have the greatest fire resistance by virtue of having the lowest weight losses.

The ASTM E 162 test results show that formulations 5, 6, and 8 gave the lowest flame spread indices, and were therefore superior on this basis to formulations 1, 2, and 7, which gave the highest flame spread indices. The flame penetration test results would credit formulation 4 with the greatest fire endurance, followed by 2, 3, 1, 6, 8, 7, and 5, in that order.

The resulting confusion can be upsetting to researcher and marketing man alike, since whether one material appears superior to another can be often decided by the choice of flammability test. The marketing man's problem, however, is relatively easy to solve: he either offers a product that is superior by the existing acceptance test, or promotes acceptance of a test that shows his product to be superior.

The researcher has a more complicated problem, since he has to rely on flammability tests not merely for comparisons of present materials, but also for trends to indicate where future work is most promising.

The vertical bar test results, for example, indicate that the addition of tetrabromoethane actually increases weight loss with formulations 2, 3 and 8; on the other hand, the ASTM E 162 test results show that tetrabromoethane reduces the flame spread index of these formulations. Relating these apparently contradictory results to combustion theory, however, yields the following conclusions: the participation of tetrabromoethane in the pyrolysis and combustion reactions of formulations 2, 3, and 8 impedes these reactions when flame travel is in the 240° direction with countercurrent air flow, but may even promote these reactions when flame

travel is in the 90° direction with concurrent air flow. Existing knowledge of the mechanisms of flame extinguishment would suggest that bromine would inhibit combustion if it were present in the combustion zone. The geometry of the vertical bar test, however, would encourage the heavier bromine to move in the 270° direction, away from the 90° direction of the flame front. The ASTM E 162 test geometry is such that bromine from the pyrolysis region would tend to move almost directly into the flame front. This particular mechanism, of course, is only one of many which have to be considered in studying the combustion of the formulations in question.

The seeming discrepancies in flammability tests are actually comparisons which, related to fundamental knowledge, can greatly increase understanding of the combustion of cellular plastics.

CONCLUSIONS

Flammability tests for cellular plastics, are, like all tests, tools which are most profitably employed when they are related to basic knowledge. The differences

between tests, and between the results of different tests, are actually comparisons which can be used to increase understanding of the flammability characteristics of these promising materials.

ACKNOWLEDGEMENT

The author expresses his appreciation to W. R. Proops and W. N. Stoops, under whose guidance and encouragement this work was done; to P. E. Burgess, Jr., and R. W. McLaughlin, who prepared the materials tested; and to W. C. Kuryla and D. H. Way, who assisted in the literature search.

LITERATURE CITED

1. American Society for Testing and Materials, Philadelphia, Pennsylvania
2. Anderson, J.J., "Retention of Flame Properties of Rigid Polyurethane Foams", Ind. & Eng. Chem., Prod, Res. & Dev. 2, 260-263 (December 1963)
3. Bono, J., "Method for Fire Tests of Floor and Ceiling Assemblies", Symposium on Fire Test Methods, ASTM STP No. 344 (October 1962)
4. Briber, A.A., "Flammability Considerations of Plastics When Used in Building and Construction", Polymer Conference Series, Wayne State University (June 1966)
5. British Standards Institution, London
6. Bruce, H.D., and Minuitti, V.P., "Small Tunnel Furnace Test for Measuring Surface Flammability", FPL Publication No. 2097 (November 1957)
7. Carpenter, D.A., "Flammability Tests for Expanded Polystyrene", British Plastics, 284-288 (May 1965)

8. Cass, R.A., Monsanto Company, private communication (March 1966)
9. Dickert, E.A., and Toone, G.C., "Chemistry and Flame Retardancy of Rigid Urethane Foams", Modern Plastics 42, No. 5, 197-204, 264-265 (January 1965)
10. Dufour, R.E., "Toxicity of Combustion and Thermal Decomposition Products of Certain Building Materials", NFPA Quarterly, 58, 31-36 (July 1964)
11. Degenkolb, J.G., "Flame Spread and Life Safety", BOCA News (April 1963)
12. Eichhorn, J., "Synergism of Free Radical Initiators with Self-Extinguishing Additives in Vinyl Aromatic Polymers", J. Appl. Polymer Sci. 8, 2497-2524 (1964)
13. Einhorn, I.N., Wayne State University, private communication (January 1967)
14. Einhorn, I.N., "Flammability Characteristics of Cellular Plastics", Polymer Conference Series, Wayne State University (May 1966)
15. Essenhigh, R.H. and Howard, J.B., "Toward a Unified Combustion Theory", Ind. & Eng. Chem. 58, No. 1, 14-23 (January 1966)

16. Factory Mutual Engineering Division, Norwood, Massachusetts
17. Fenimore, C.P., and Martin, F.J., "Flammability of Polymers", Combustion and Flame 10, No. 2, 135-139 (June 1966)
18. Fenimore, C.P., "Flammability of Polymers", Polymer Conference Series, Wayne State University (June 1966)
19. Ferrigno, T.H., "Rigid Plastics Foams", Reinhold Publishing Corp. (1963)
20. Feuer, S.S., and Torres, A.F., "Flame Resistance Testing of Plastics", Chem. Eng. 69, No. 7, 138-142 (April 1962)
21. Friedman, R., and Levy, J.B., "Survey of Fundamental Knowledge of Mechanisms of Action of Flame-Extinguishing Agents", WADC Technical Report 56-568, ASTIA Document No. AD 110685 (January 1957)
22. Friedman, R., and Levy, J.B., "Survey of Fundamental Knowledge of Mechanisms of Action of Flame-Extinguishing Agents: First Supplementary Report, WADC Technical Report 56-568 Supplement 1, ASTIA Document No. AD 208317 (September 1958)

23. Gross, D., and Loftus, J.J., "Flame Spread Properties of Building Finish Materials", ASTM Bulletin, No. 230, 56-60 (May 1958)
24. Gross, D., and Loftus, J.J., "Surface Flammability of Cellular Plastic Foams", NBS Report No. 7325 (August 1961)
25. Hilado, C.J., "Effects of Flame Variation in ASTM D 1692 Flammability Test", J. Cellular Plastics, in press
26. Hilado, C.J., "Computer Applications in Materials Evaluation Programs", Ind. & Eng. Chem., Prod. Res. & Dev. 5, No. 4, 301-305 (December 1966)
27. Hooker Chemical Corporation, "Intermittent Flame Test" (September 1955)
28. Jacobson, M., Nagy, J., and Cooper, A.R., "Explosibility of Dusts Used in the Plastics Industry", U.S. Bureau of Mines Report No. 5971 (1962)
29. Jackson, D.E., Butler Manufacturing Company, private communication (February 1967)

30. Kelleher, P.G., Bell Telephone Laboratories, private communication (November 1966)
31. Levy, M.M., "A Simplified Method for Determining Flame Spread", SPE Annual Technical Conference (March 1966)
32. Mitchell, D.W., Murphy, E.M., and Nagy, J., "Fire Hazard of Urethane Foam in Mines", U.S. Bureau of Mines Report No. 6837 (1966)
33. Nametz, R.C., Deanin, R.D., and Lambert, P.M., "Flame-Resistant Rigid Polyurethane Foams from Monobrominated Toluene Diisocyanate", SPE Transactions, 251-255 (October 1964)
34. National Aniline Div. of Allied Chemical Corp., "National Aniline Test Method", CF-TM-11 (September 1959)
35. National Fire Protection Association, Boston, Massachusetts
36. Patten, G.A., "Ignition Temperatures of Plastics", Modern Plastics 38, No. 11, 119-120, 122, 180 (July 1961)

37. Peters, C.C., and Eickner, H.W., "Surface Flammability as Determined by the FPL 8-Foot Tunnel Method", Symposium on Fire Test Methods, ASTM STP No. 344 (October 1962)
38. Piechota, H., "Some Correlations between Raw Materials, Formulation, and Flame-Retardant Properties of Rigid Urethane Foams", J. Cellular Plastics 1, No. 1, 186-199 (January 1965)
39. Rohm & Haas Co., "A Method of Measuring Smoke Density", NFPA Quarterly, 276-287 (January 1964)
40. Robertson, A.F., Gross, D., and Loftus, J., "A Method for Measuring Surface Flammability of Materials Using a Radiant Energy Source", ASTM Proceedings 56, 1437-1453 (1956)
41. Robertson, A.F., "Surface Flammability Measurements by the Radiant Panel Method", Symposium on Fire Test Methods, ASTM STP No. 344 (October 1962)
42. Sauber, W. J., and Patten, G. A., "Flammability Tests for Plastics", Plastics World (December 1960)

43. Saunders, J.H., and Backus, J.K., "Thermal Degradation and Flammability of Urethan Polymers", Rubber Chem. & Tech. 39, No. 2, (March 1966)
44. Schael, G.W., Upjohn Company, private communication (November 1966)
45. Setchkin, N.P., "A Method and Apparatus for Determining the Ignition Characteristics of Plastics", J. Res. NBS 43, 591-608 (December 1949)
46. Slezak, F.B., Stallings, J.P., and Rosen, I., "Chlorinated Xylene Derivatives for Flame Retardant Rigid Polyurethane Foams", Ind. & Eng. Chem., Prod. Res. & Dev. 3, 292-294 (December 1964)
47. Stengard, R.A., "Properties of Rigid Urethane Foams", Du Pont Bulletin (June 1963)
48. Stewart, S.A., "Simulated Test Method for Reproducing Theoretical Conditions Encountered in an Unexplained Fire in a Railroad Caboose under Construction", Martin Sweets Company (August 1964)

49. Thompson, N.J., and Cousins, E.W., "The FM Construction Materials Calorimeter", NFPA Quarterly, 186-192 (January 1959)
50. Underwriters Laboratories Inc., Northbrook, Illinois
51. U.S. Dept. of Commerce, Federal Test Method Standards
52. U.S. General Services Administration, Federal Specifications
53. Vandersall, H.L., "The Two-Foot Flame Tunnel: Its Use in the Laboratory Evaluation of Fire Resistance and Retardance", Monsanto Special Report No. 6717 (May 1966)
54. Way, D.H., Union Carbide Corporation, private communication (January 1967)
55. Wilson, J.A., "Surface Flammability of Materials: A Survey of Test Methods and Comparison of Results", Symposium on Fire Test Methods, ASTM STP No. 301 (February 1961)
56. Yuill, C.H., "Flame-Spread Tests in a Large Tunnel Furnace", Symposium on Fire Test Methods, ASTM STP No. 344 (October 1962)

FIGURE 1. SURFACE POSITIONS IN FLAMMABILITY TESTS

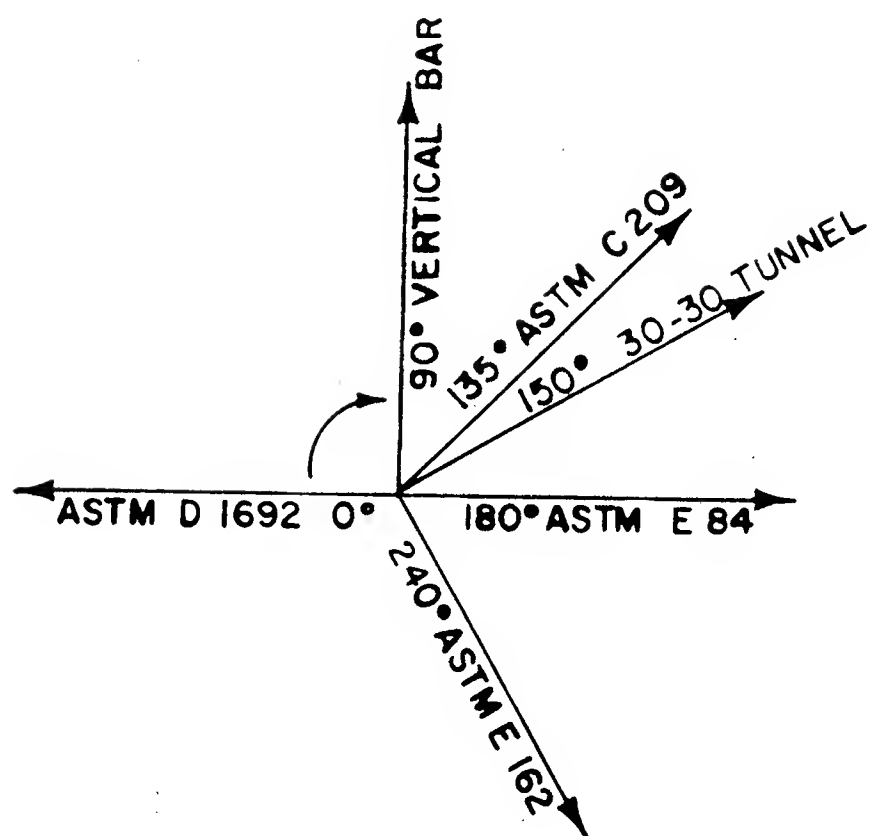


FIGURE 2. ASTM D 1692 TEST GEOMETRY

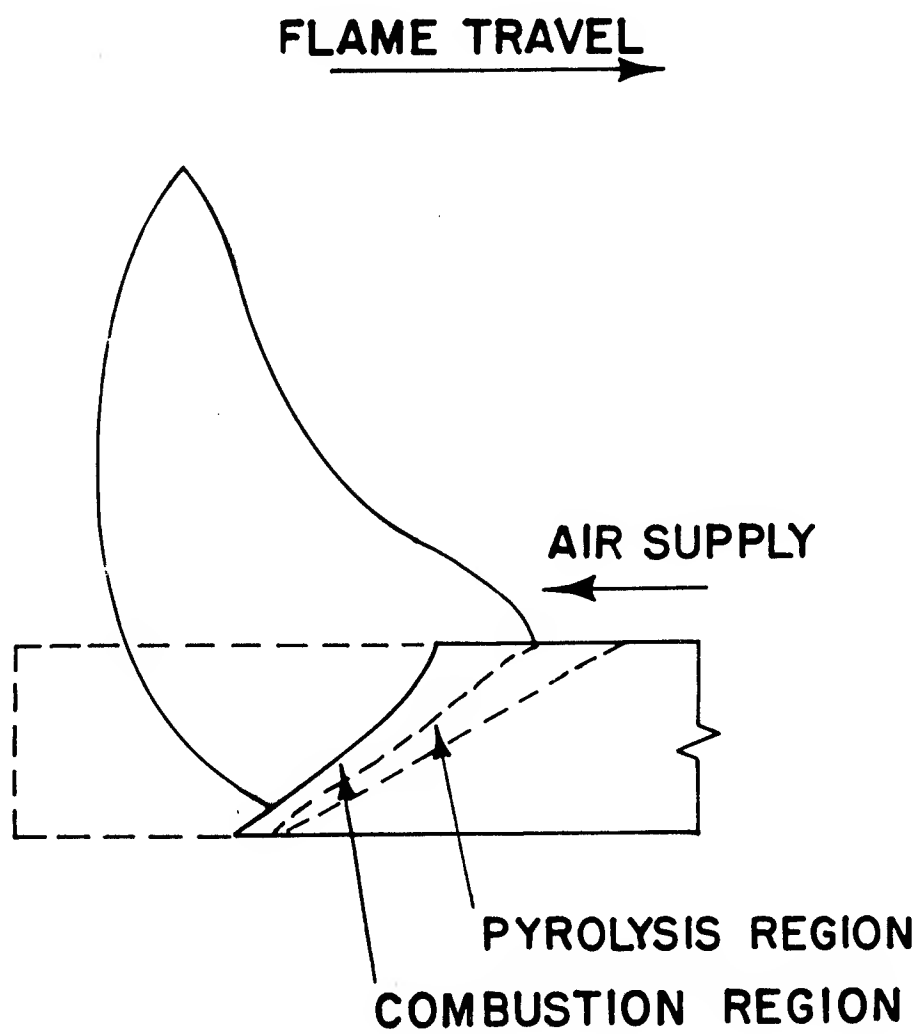


FIGURE 3. VERTICAL BAR TEST GEOMETRY

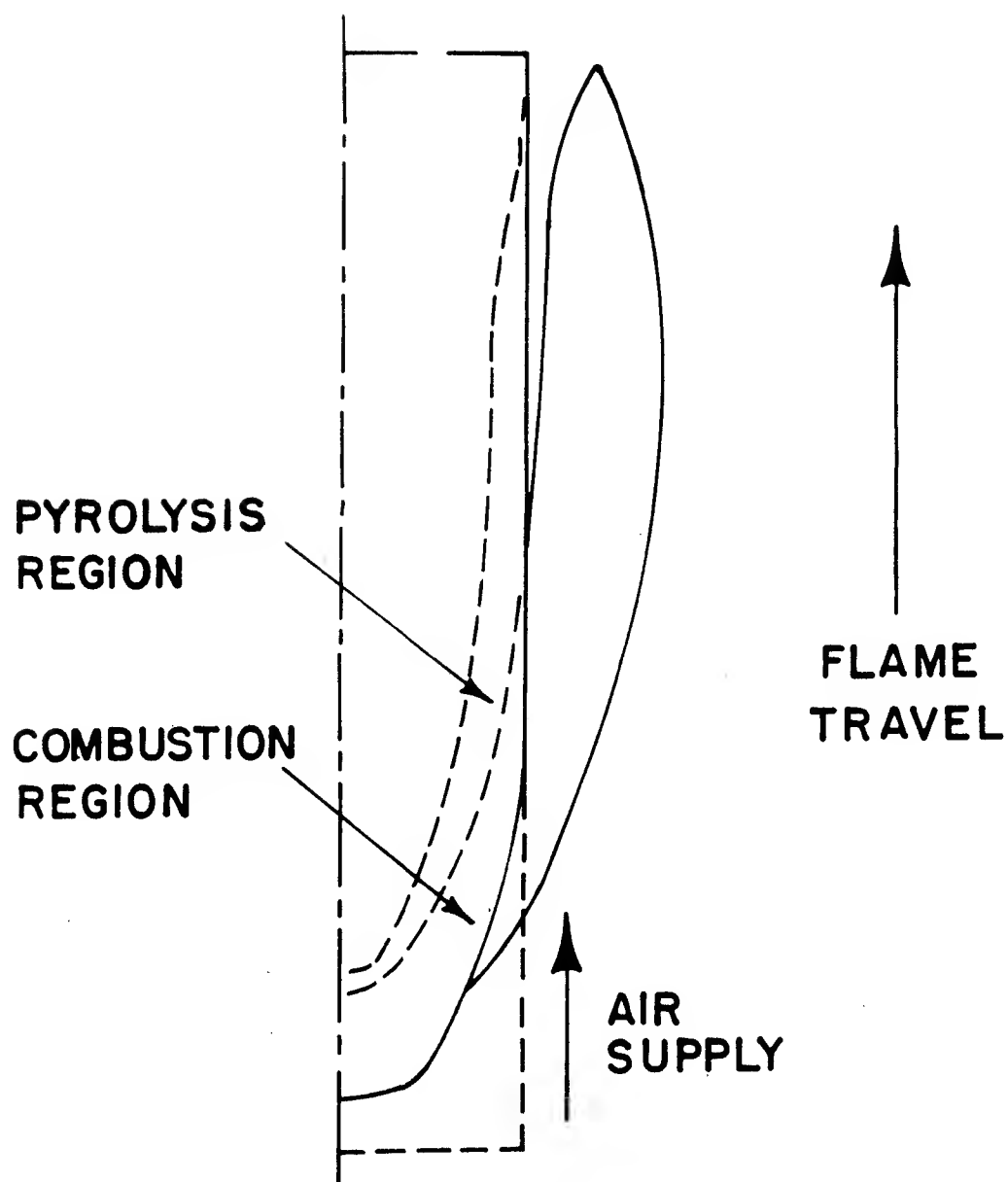


FIGURE 4. ASTM E 162 TEST GEOMETRY

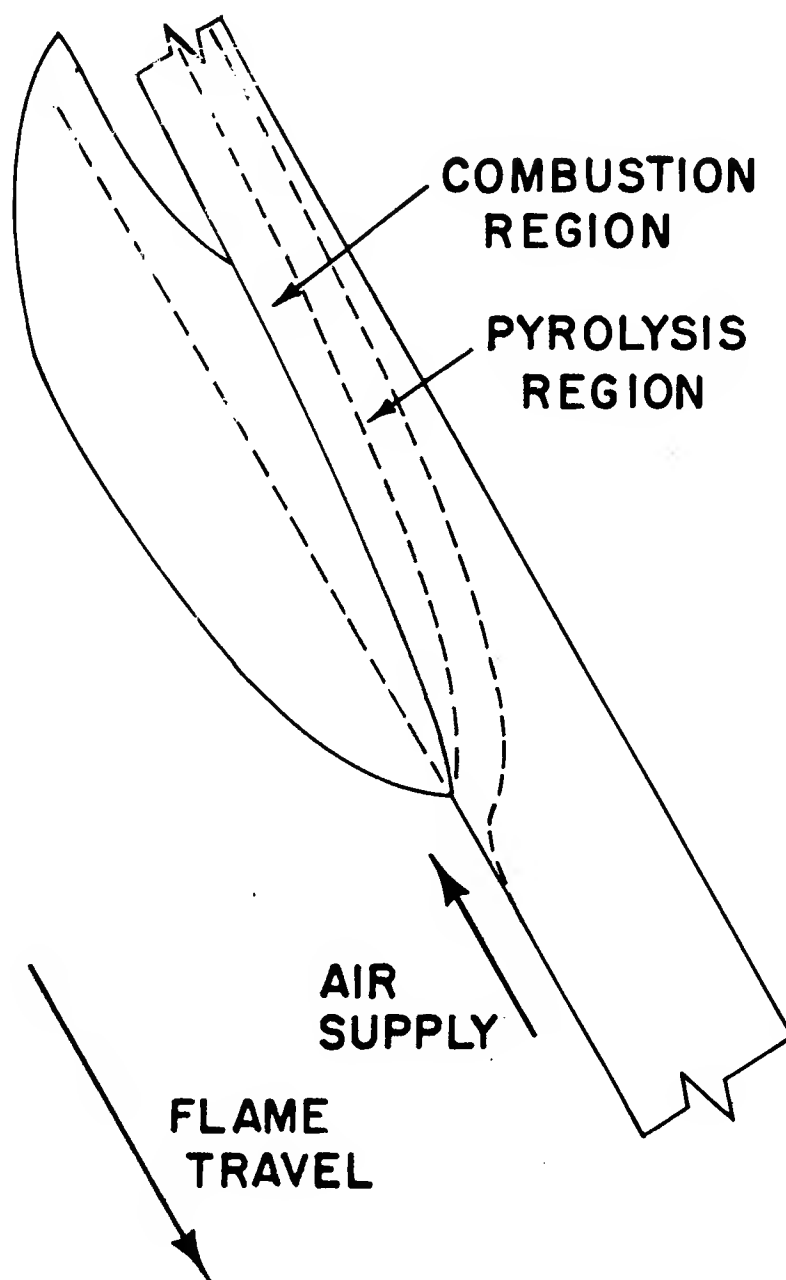


FIGURE 5. FLAME PENETRATION TEST GEOMETRY

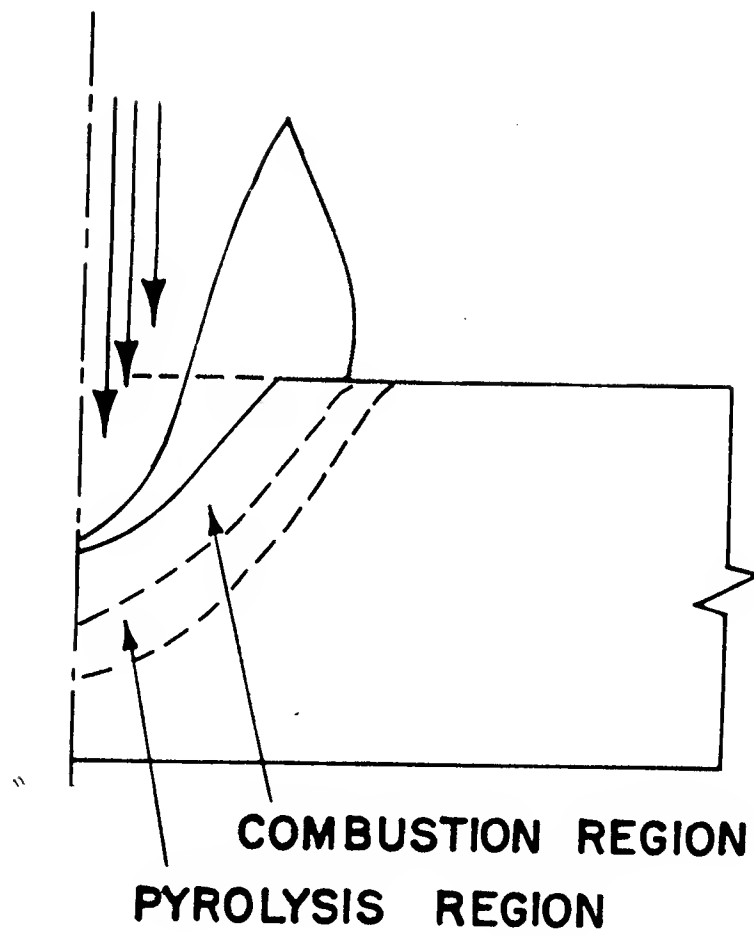


FIGURE 6. EFFECT OF FLAME RETARDANT ADDITIVE CONCENTRATION
ON ASTM D 1692 BURNING EXTENT

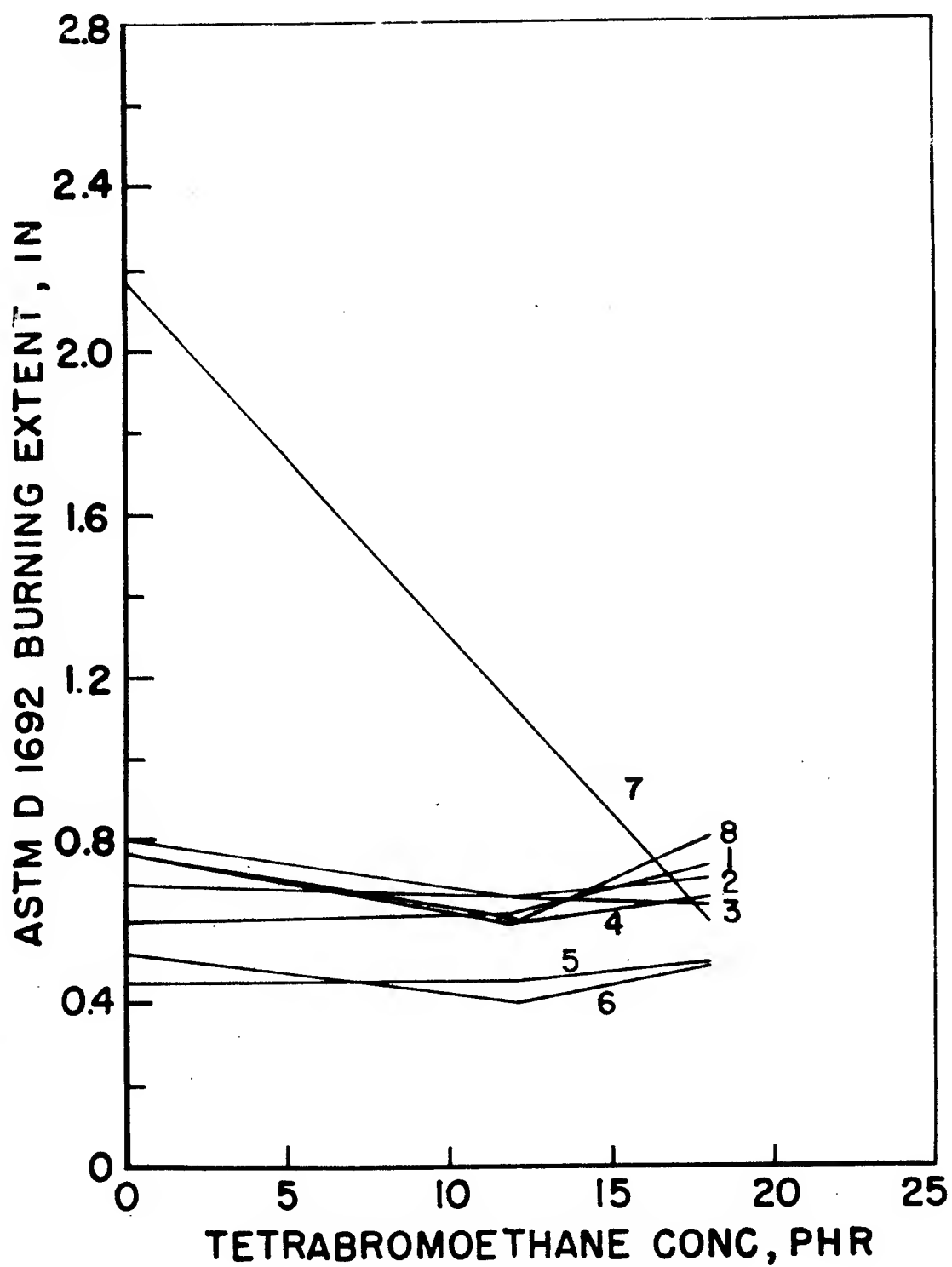


FIGURE 7. EFFECT OF FLAME RETARDANT ADDITIVE CONCENTRATION ON ASTM D 1692 BURNING EXTENT

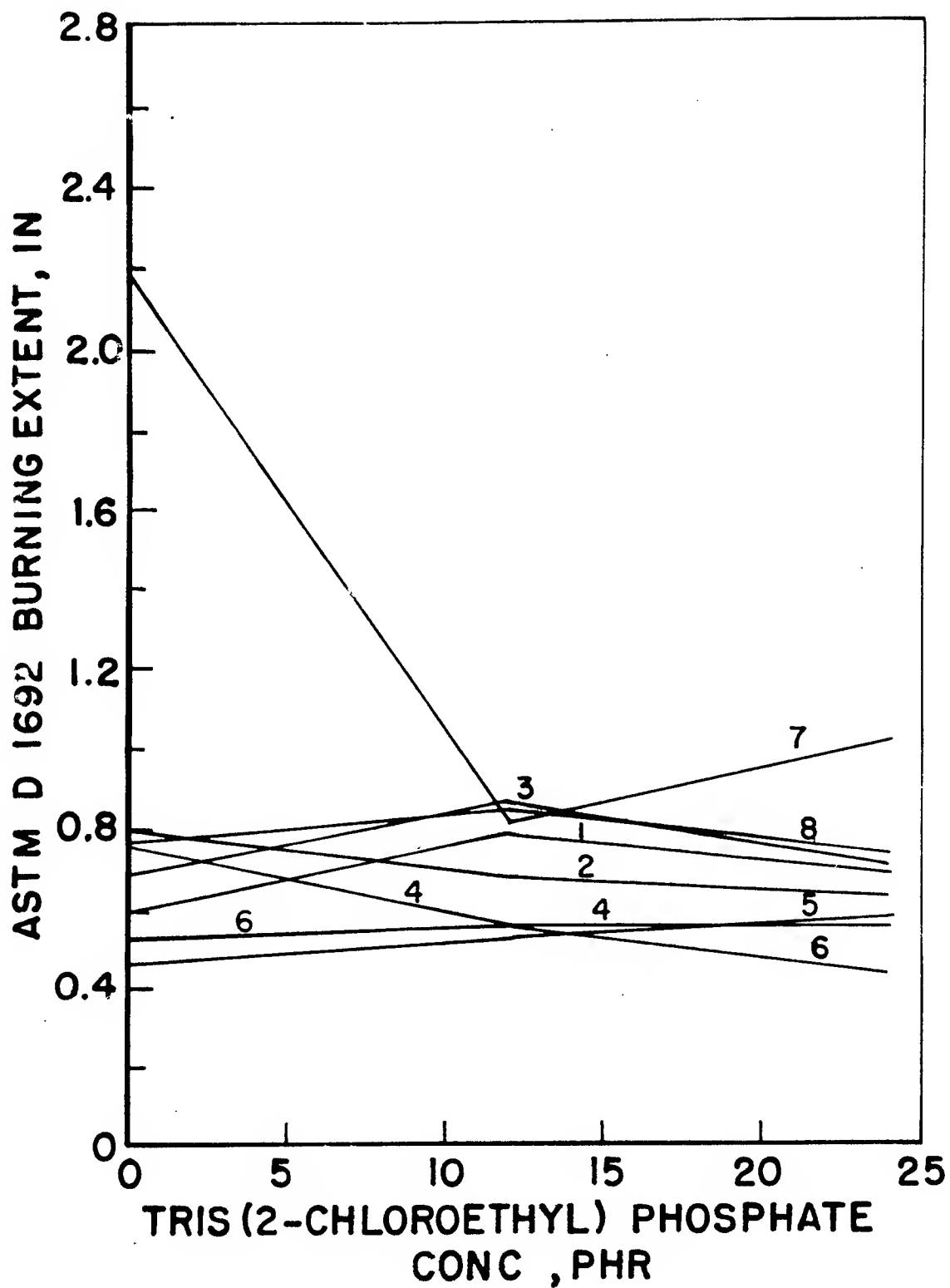


FIGURE 8. EFFECT OF FLAME RETARDANT ADDITIVE CONCENTRATION ON ASTM D 1692 BURNING EXTENT

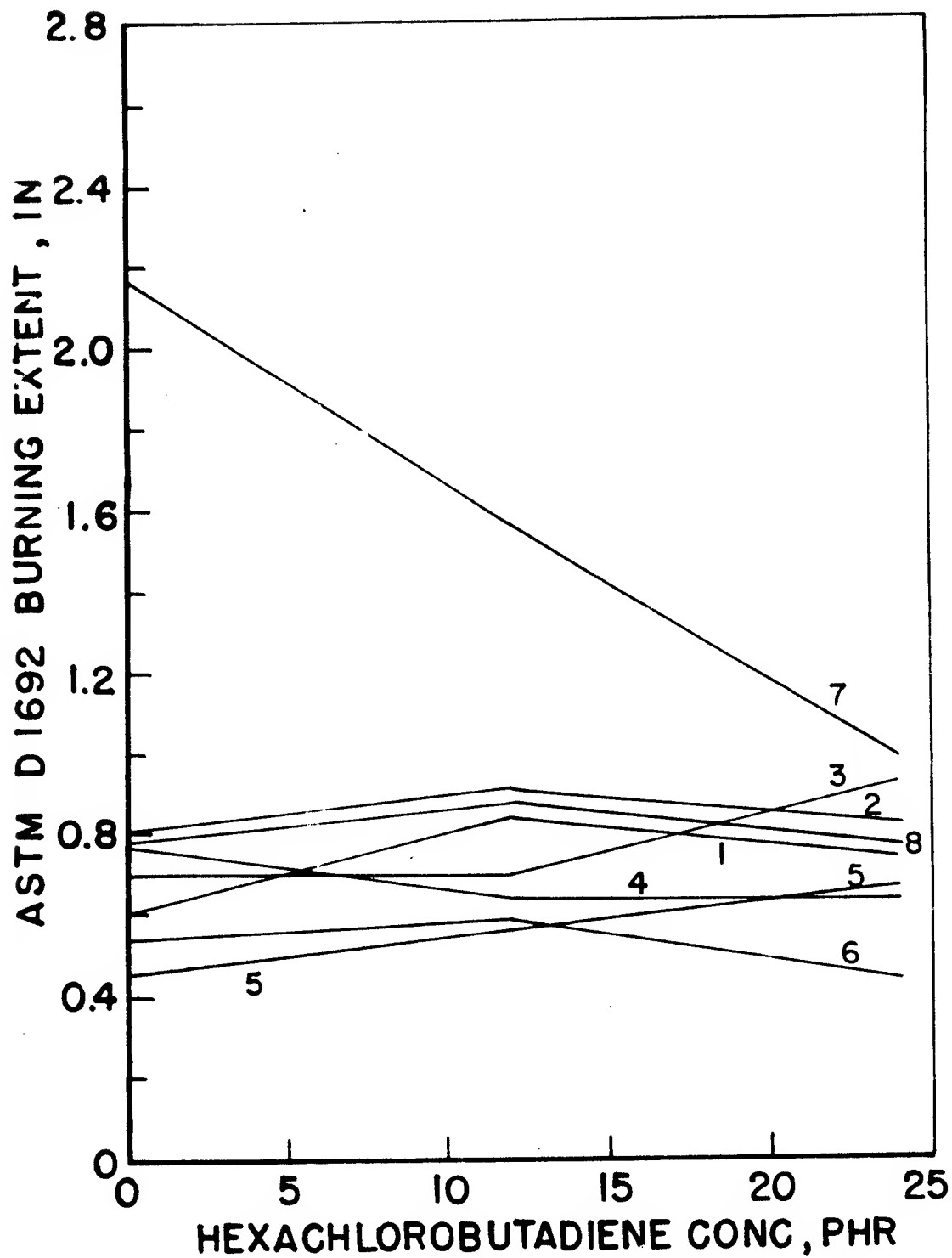


FIGURE 9. EFFECT OF FLAME RETARDANT ADDITIVE CONCENTRATION ON ASTM D 1692 BURNING EXTENT

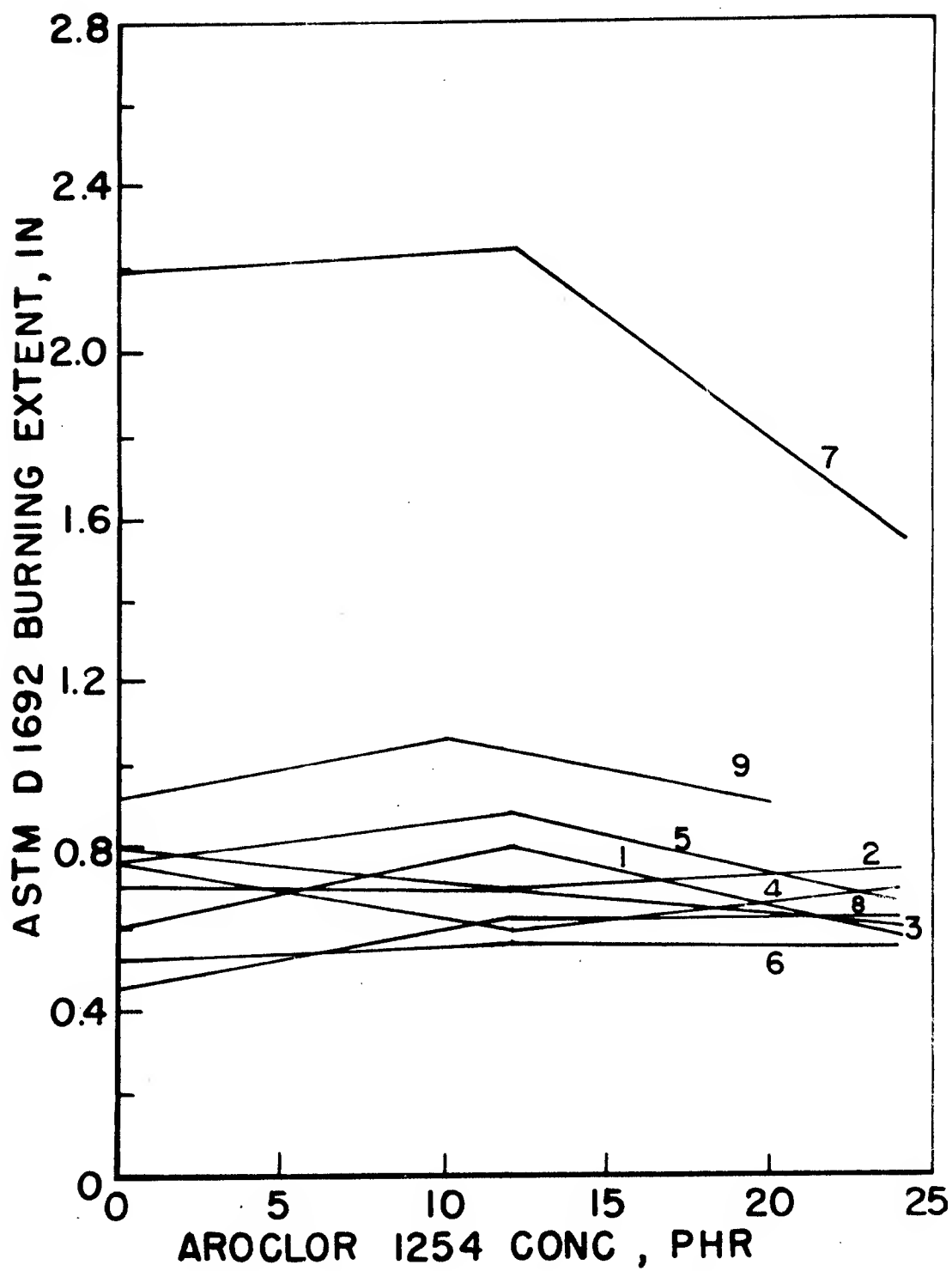


FIGURE 10. EFFECT OF FLAME RETARDANT ADDITIVE CONCENTRATION ON VERTICAL BAR WEIGHT LOSS

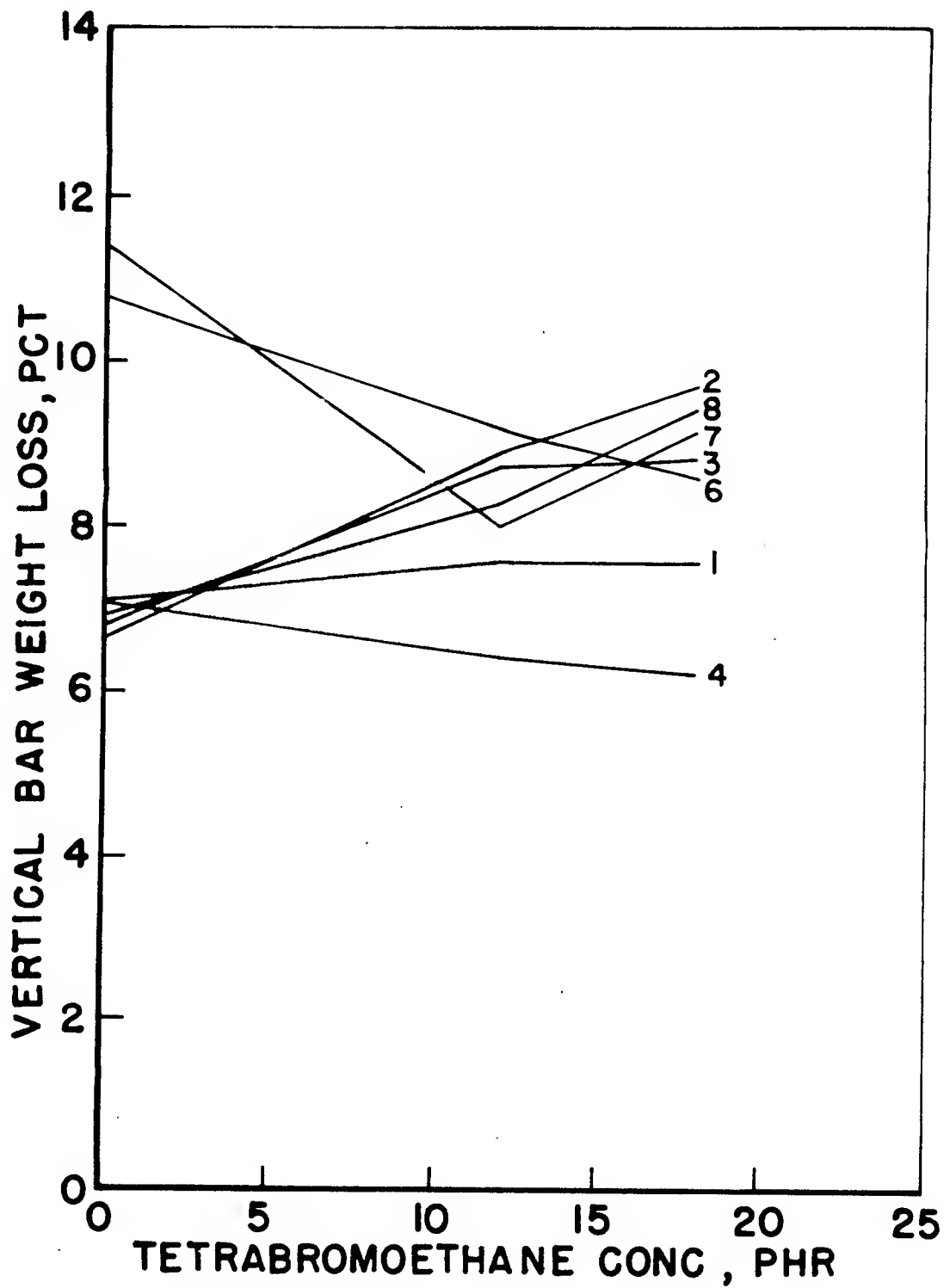


FIGURE 11. EFFECT OF FLAME RETARDANT ADDITIVE CONCENTRATION ON VERTICAL BAR WEIGHT LOSS

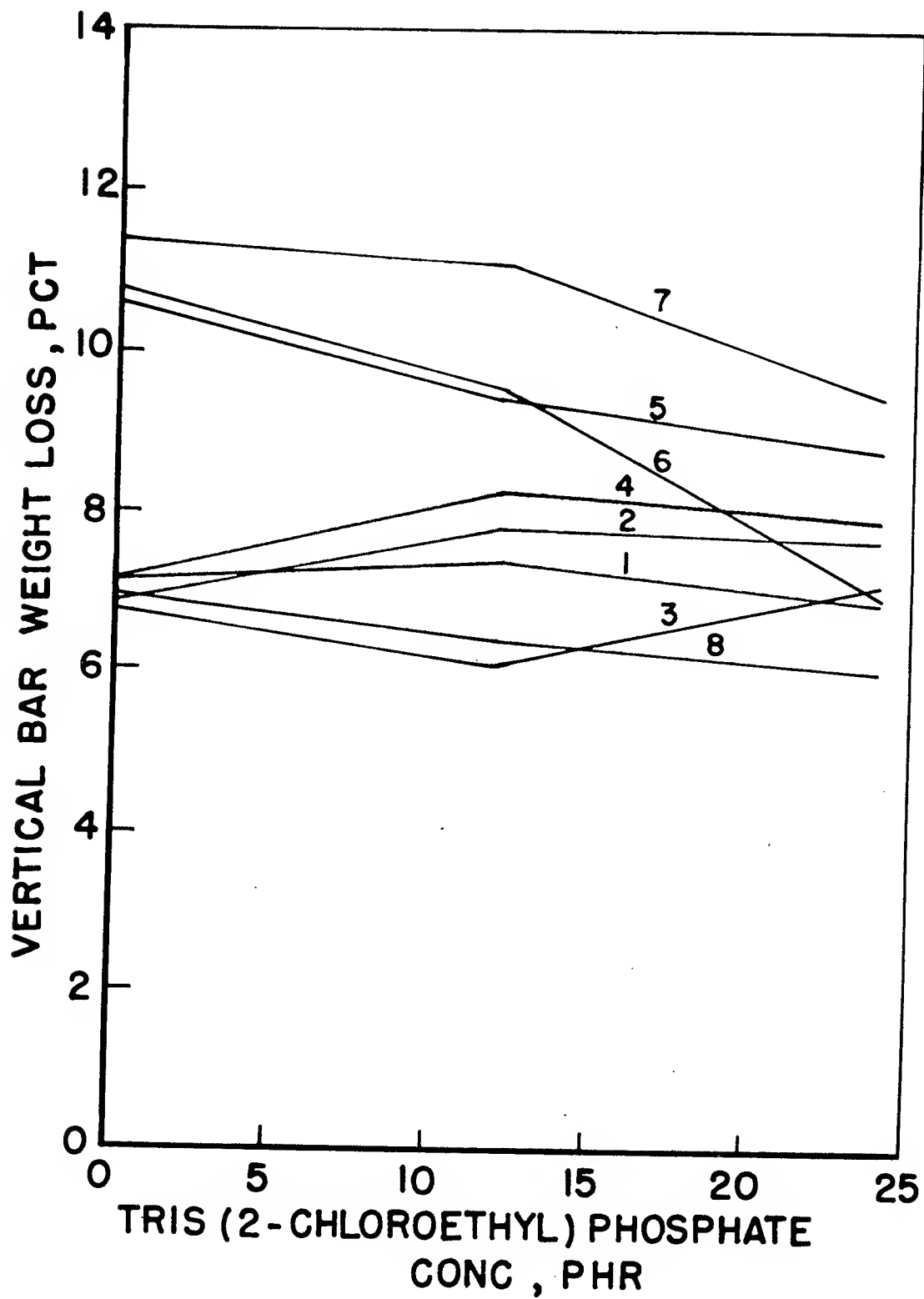


FIGURE 12. EFFECT OF FLAME RETARDANT ADDITIVE CONCENTRATION ON VERTICAL BAR WEIGHT LOSS

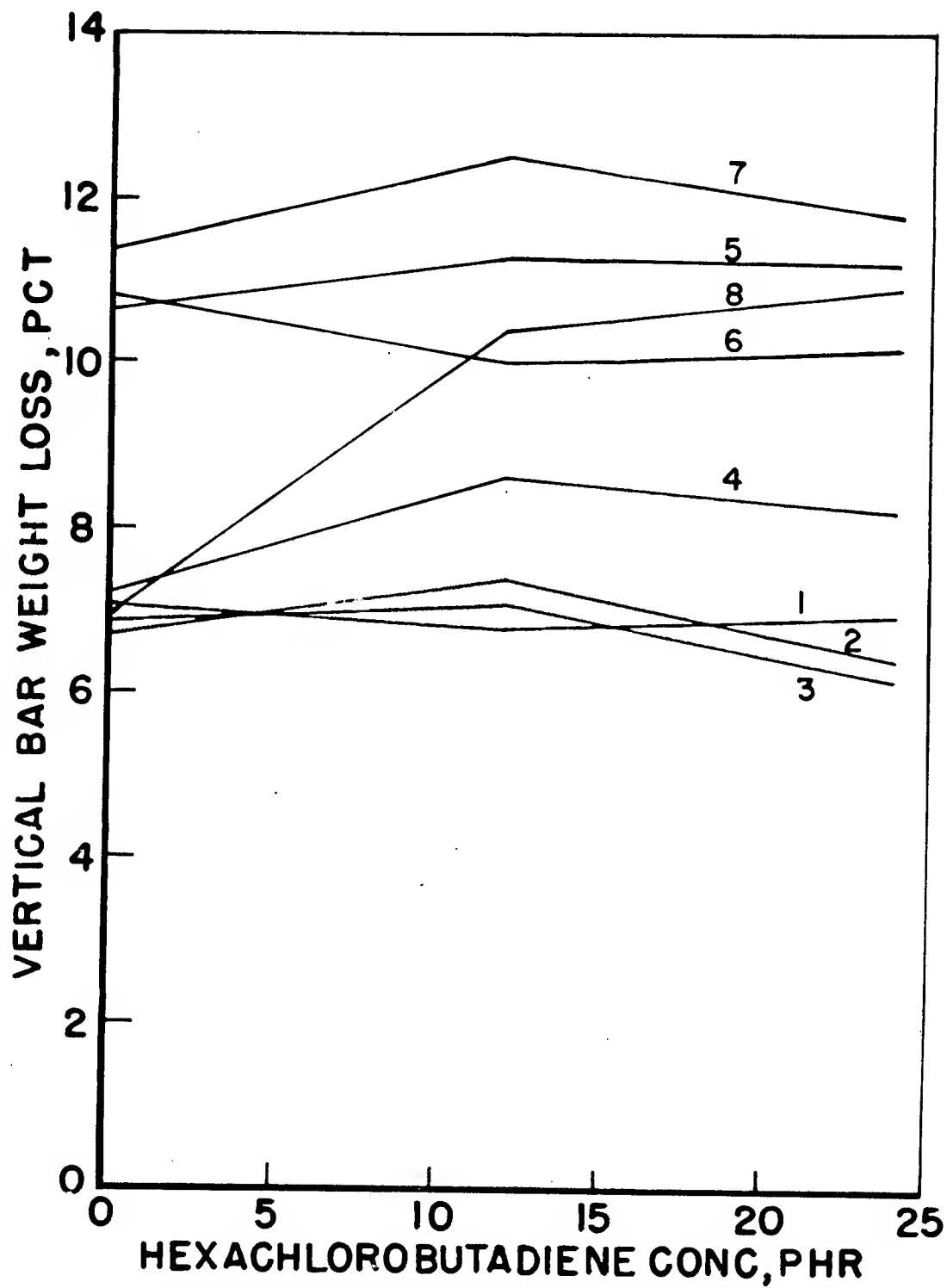


FIGURE 13. EFFECT OF FLAME RETARDANT ADDITIVE CONCENTRATION ON VERTICAL BAR WEIGHT LOSS

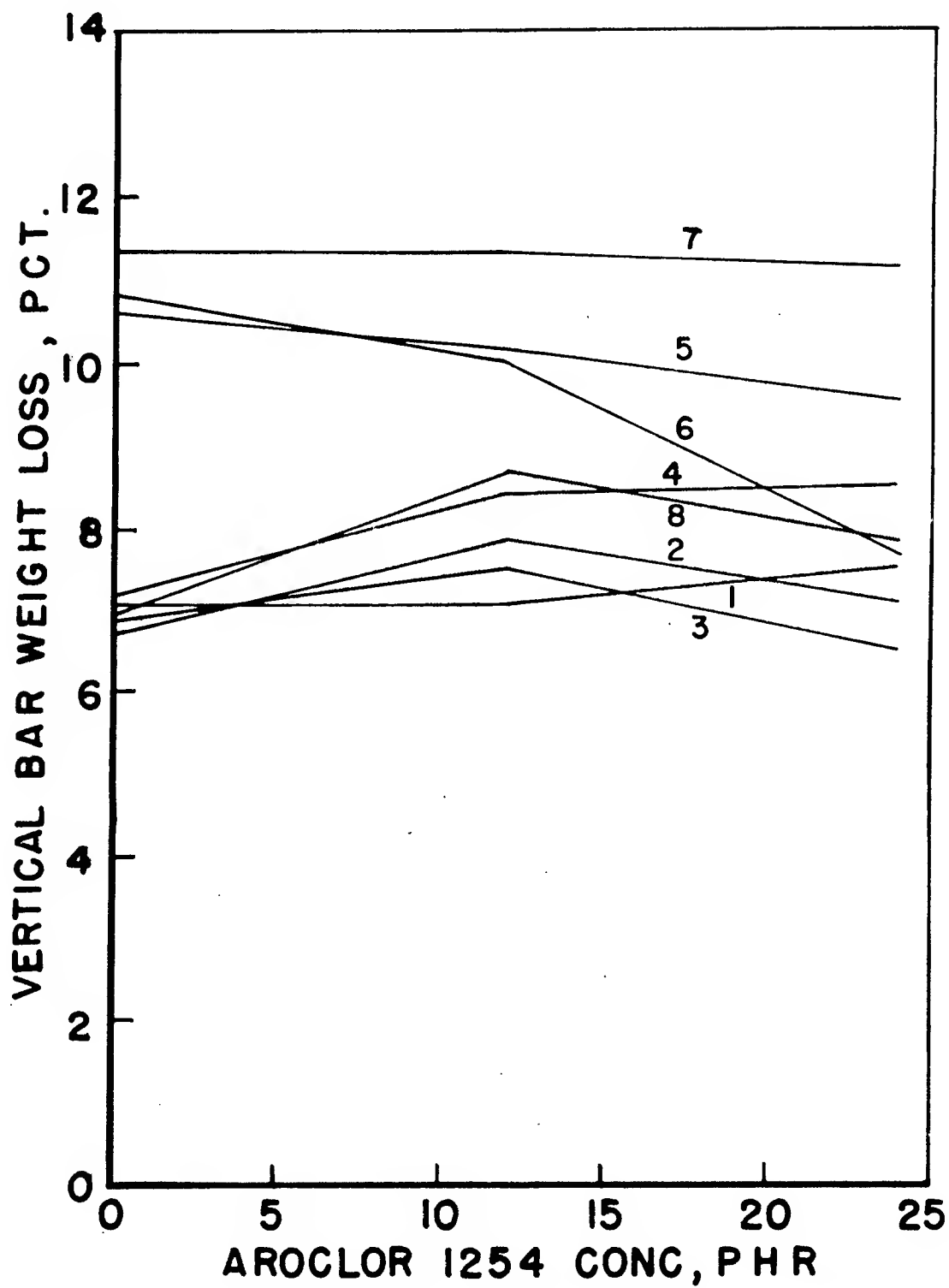


FIGURE 14. EFFECT OF FLAME RETARDANT ADDITIVE CONCENTRATION
ON ASTM E 162 FLAME SPREAD INDEX

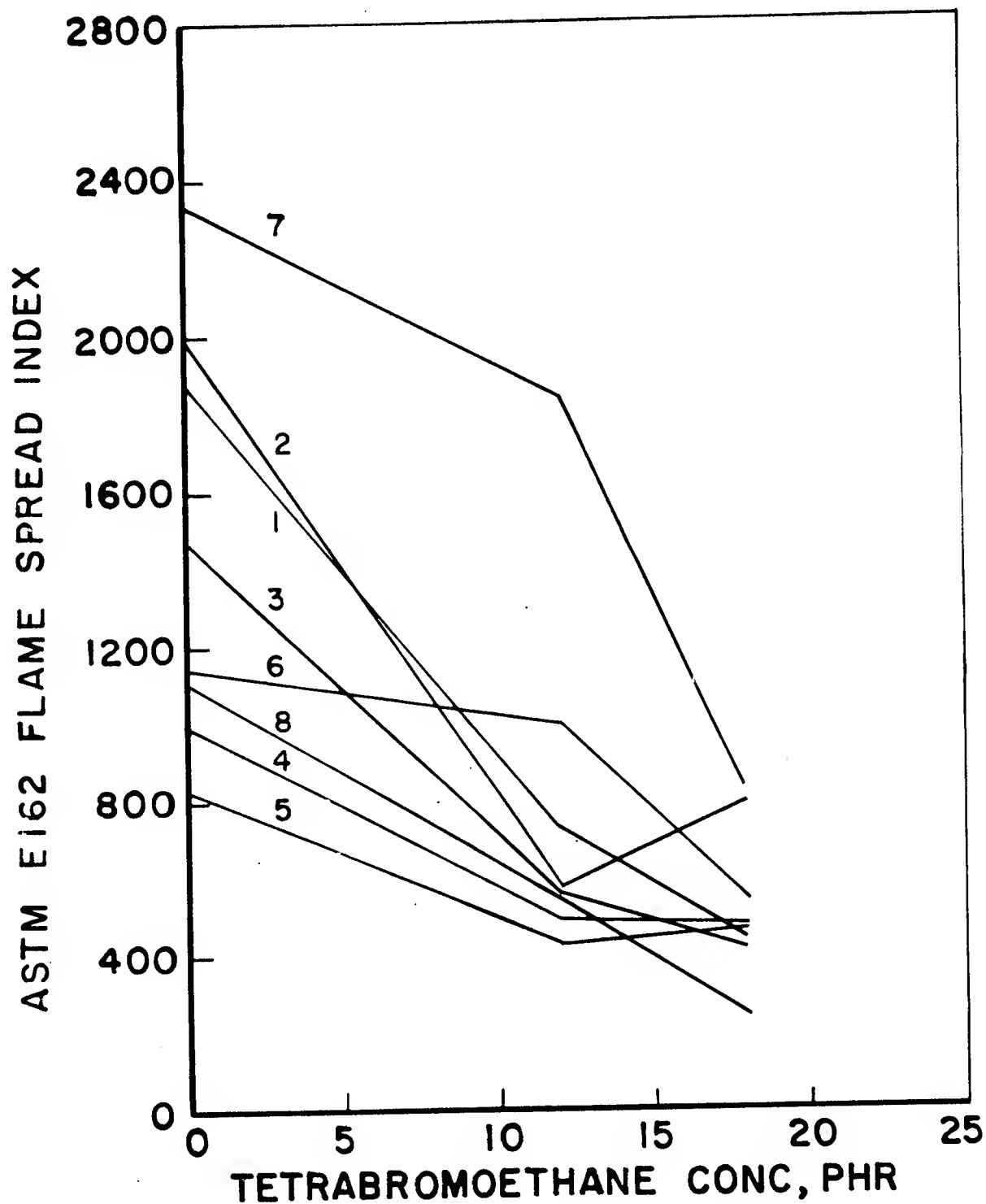


FIGURE 15. EFFECT OF FLAME RETARDANT ADDITIVE CONCENTRATION ON ASTM E 162 FLAME SPREAD INDEX

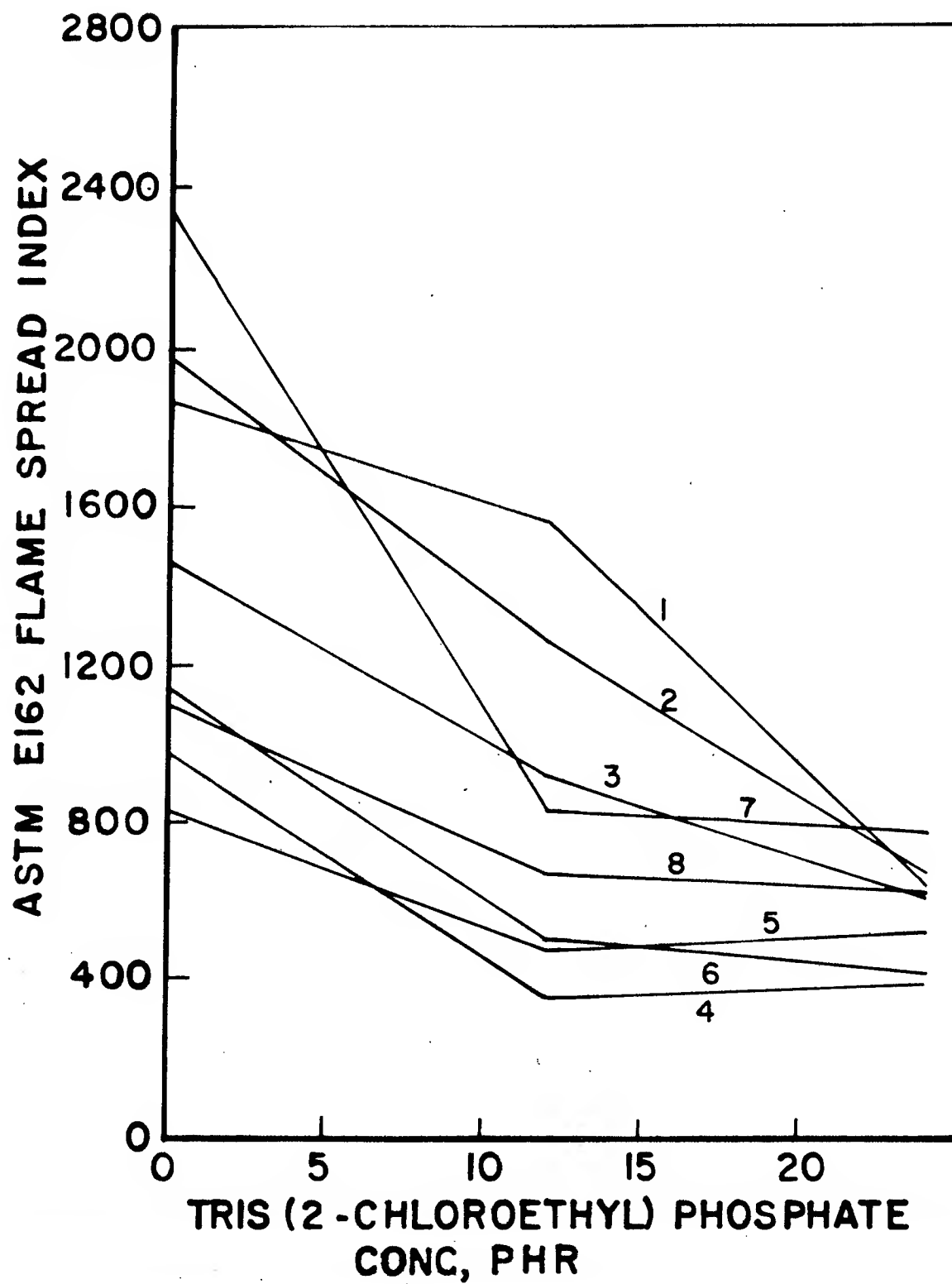


FIGURE 16. EFFECT OF FLAME RETARDANT ADDITIVE CONCENTRATION
ON ASTM E 162 FLAME SPREAD INDEX

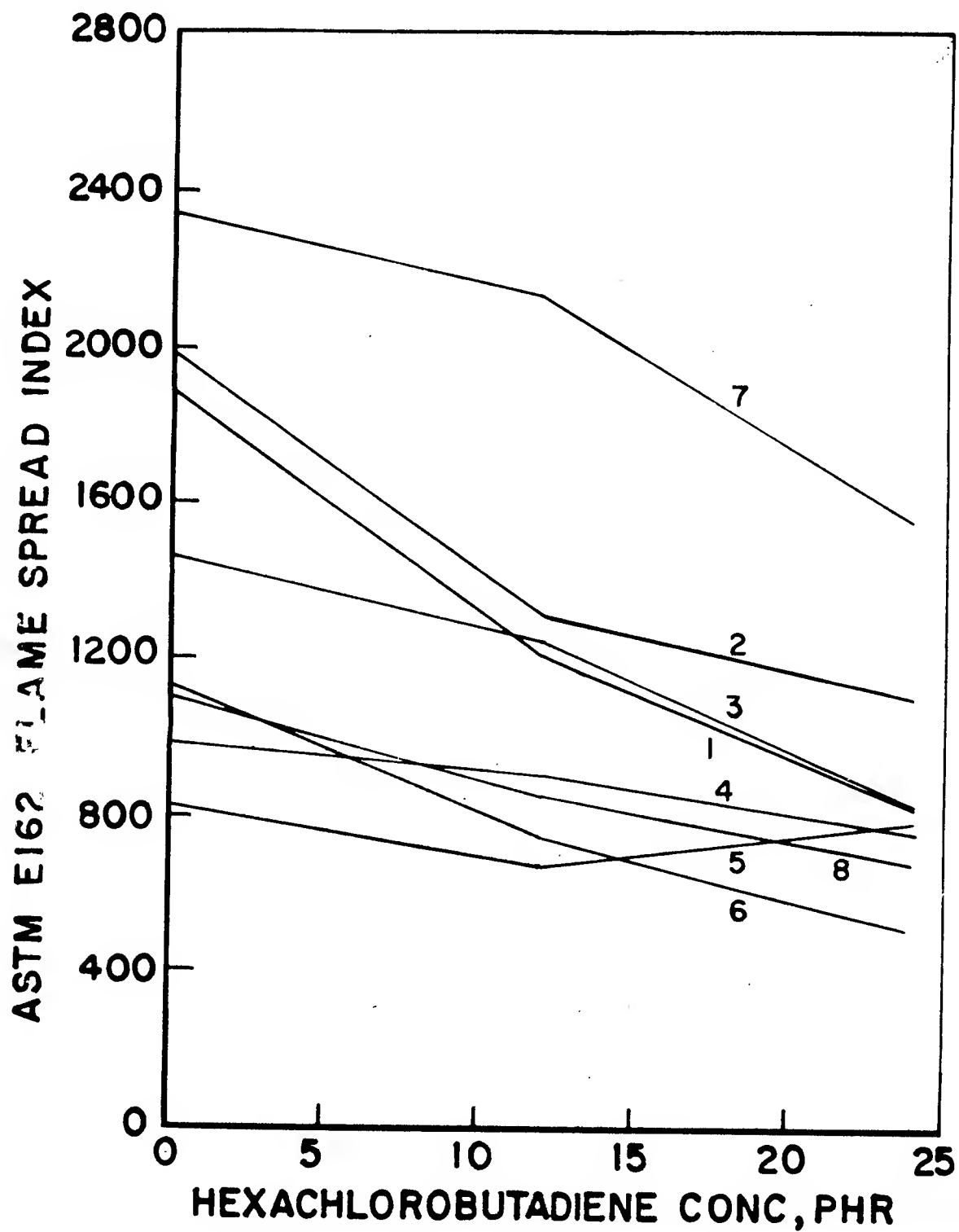


FIGURE 17. EFFECT OF FLAME RETARDANT ADDITIVE CONCENTRATION ON ASTM E 162 FLAME SPREAD INDEX

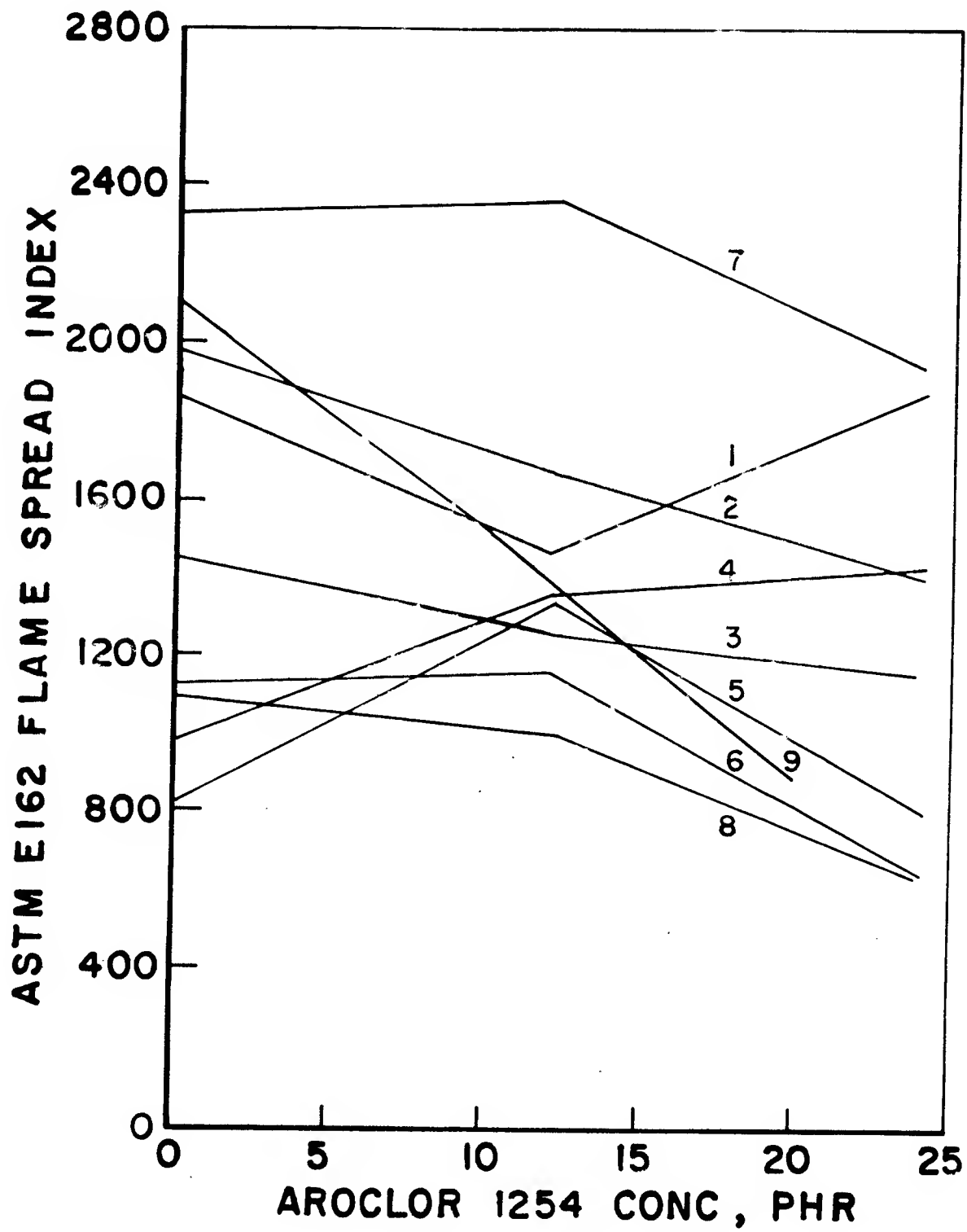


FIGURE 18. EFFECT OF FLAME RETARDANT ADDITIVE CONCENTRATION ON FLAME PENETRATION TIME

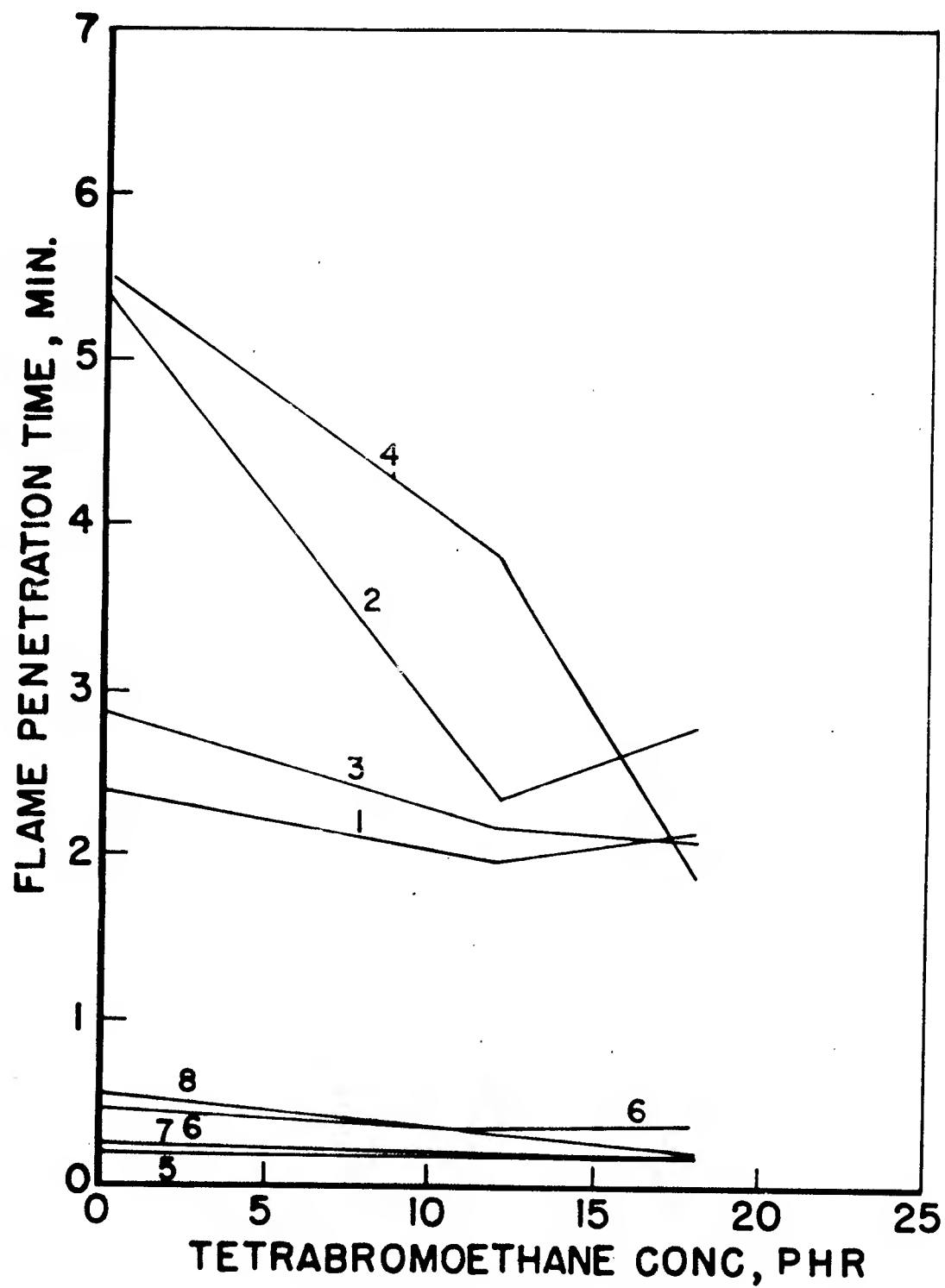


FIGURE 19. EFFECT OF FLAME RETARDANT ADDITIVE CONCENTRATION ON FLAME PENETRATION TIME

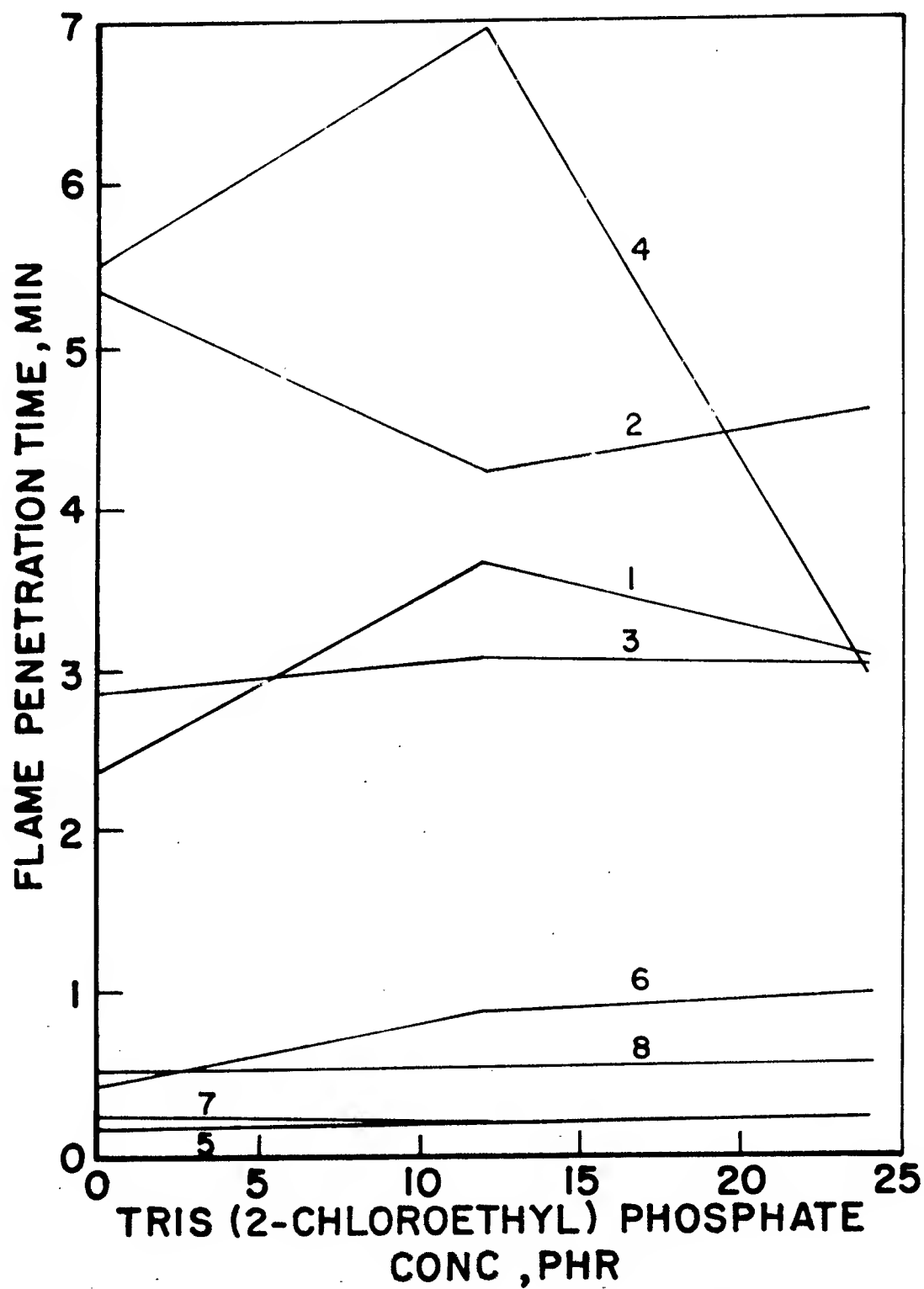


FIGURE 20. EFFECT OF FLAME RETARDANT ADDITIVE CONCENTRATION
ON FLAME PENETRATION TIME

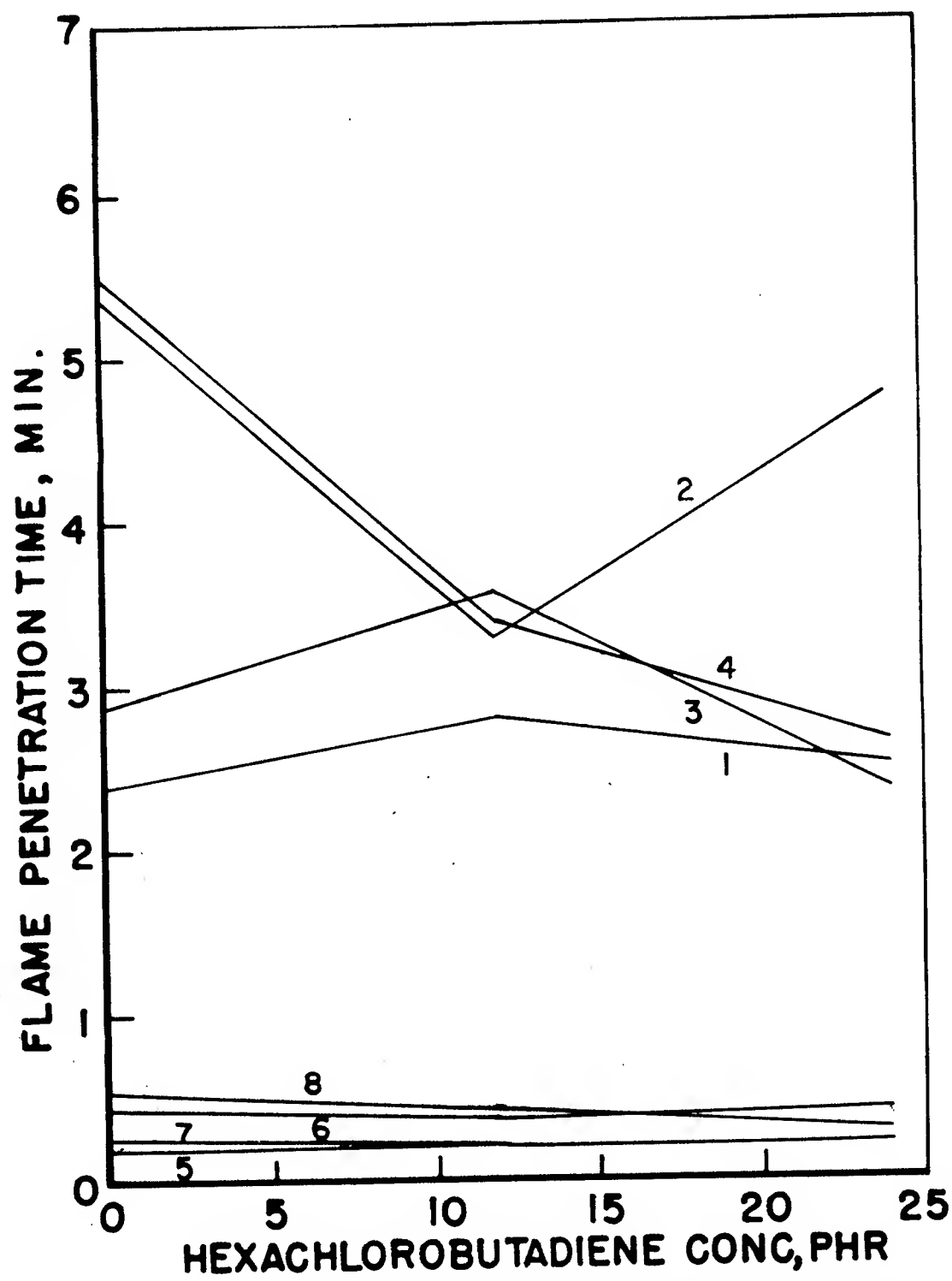
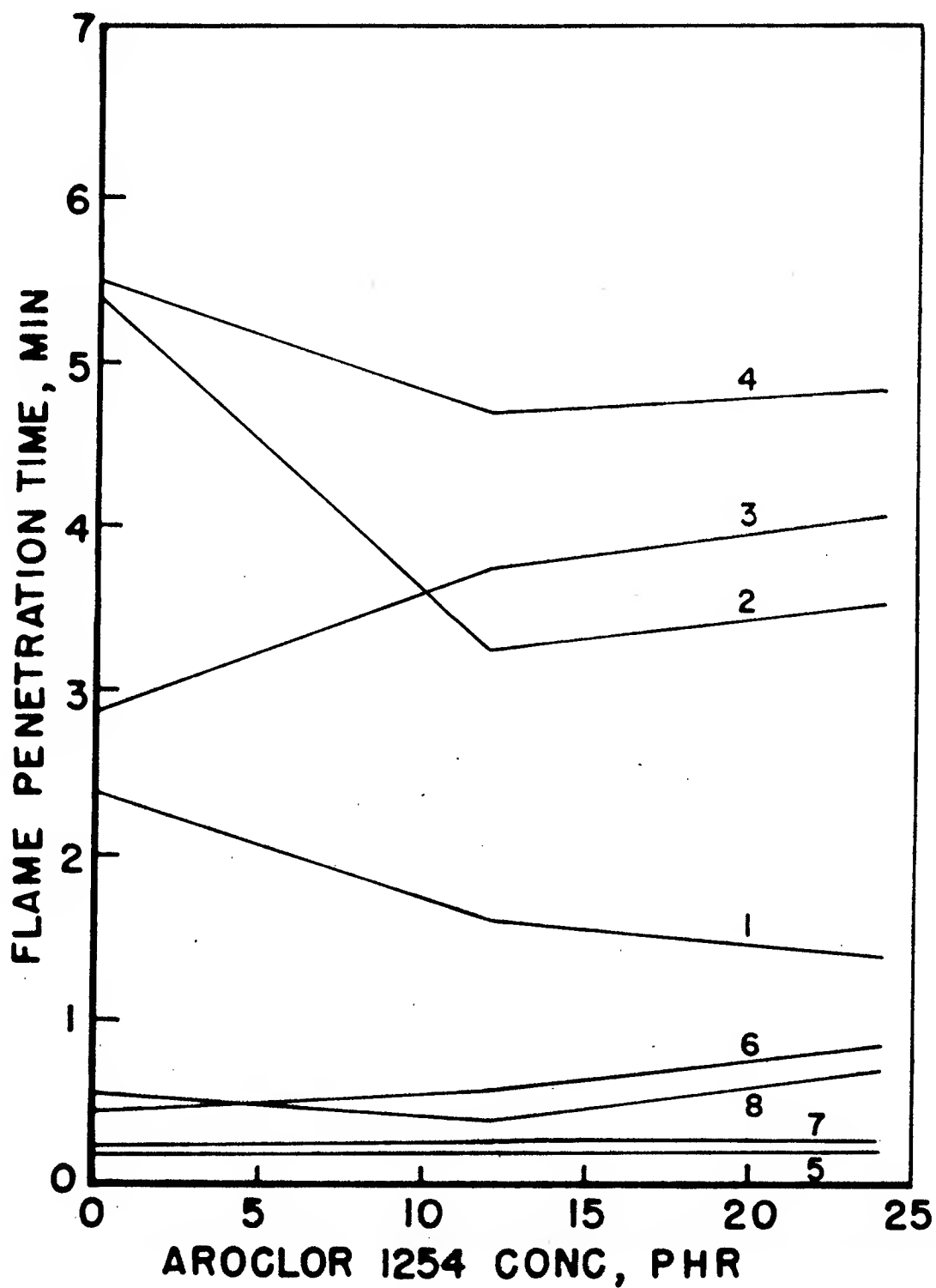


FIGURE 21. EFFECT OF FLAME RETARDANT ADDITIVE CONCENTRATION ON FLAME PENETRATION TIME



10214-08

SMOKE DEVELOPMENT IN URETHANE FOAMS

By

I. N. Einhorn, R. W. Mickelson
B. Shah and D. Luk

Department of Chemical Engineering
Wayne State University

SMOKE DEVELOPMENT IN URETHANE FOAMS

Introduction

Considerable research has been directed toward the development of foaming systems possessing reduced flame propagation characteristics. Current research conducted within the Department of Chemical Engineering of Wayne State University has indicated that the incorporation of flame retardants into urethane foams, while producing slower flame propagation rates, vastly increases the development of smoke and the concentrations of toxic pyrolytic decomposition products.

In the present program, a series of flexible and rigid urethane foams were prepared and subjected to combustion under laboratory conditions. The parameters pertaining to combustion were characterized by the use of differential thermal analysis, thermal gravimetric analysis, infrared spectrophotographic analysis, and burning in a small scale smoke chamber.

Theoretical Considerations of Factors Relating to Combustion

A generalized mechanism for the combustion of polymeric materials has been proposed by Buck⁽¹⁾ as follows:

"In the combustion of any polymer, decomposition first occurs as the result of heat supplied from a source. At the same time, any combustible gases from this decomposition are heated to their ignition temperatures and if an adequate oxidizing agent is present, these gases ignite. This burning provides additional heat to propagate further decomposition and ignition. The simple requirements for a flame then are heat, a material which will provide combustible gases, and an oxidizing agent."

Other materials resulting from the pyrolytic decomposition (in addition to combustible gases) are non-combustible gases such as water, carbon dioxide, or a hydrogen halide, and a carbonaceous char. Saunders⁽²⁾ illustrated this process by the diagrammatic representation shown in Figure 1.

The evolution of non-combustible gases which may be formed during combustion tend to reduce burning by several mechanisms:

- (1) The heavy gases may shield the oxidizer from the burning mass.
- (2) All non-combustible gases help dissipate the heat and cool the fire.
- (3) The latent heat of vaproization of water tends to reduce the temperature.

The formation of a carbonaceous char during burning will act as an insulation to reduce the rate of heat penetration to the unburned underlying material.

The flammability characteristics of cellular plastics may be correlated with energy relationships within the polymer. The most important energy factors are cohesive energy, hydrogen bonding, heat of combustion, and bond dissociation energy. (3,4,5,6)

The effect of elemental constituents on the flammability characteristics of cellular plastics has been reported in the literature. (7,8,9,10,11) Compounds containing the elements: phosphorous, bromine, chlorine, antimony (preferable as an oxide), boron, and nitrogen reduce flame propagation of polymeric materials. Consideration must be given to the mechanism by which the flame retardant is incorporated into the final polymeric structure. If the elemental constituents are part of a chemically reactive compound, they become an integral part of the final polymer. It is desirable to build these elements into a position

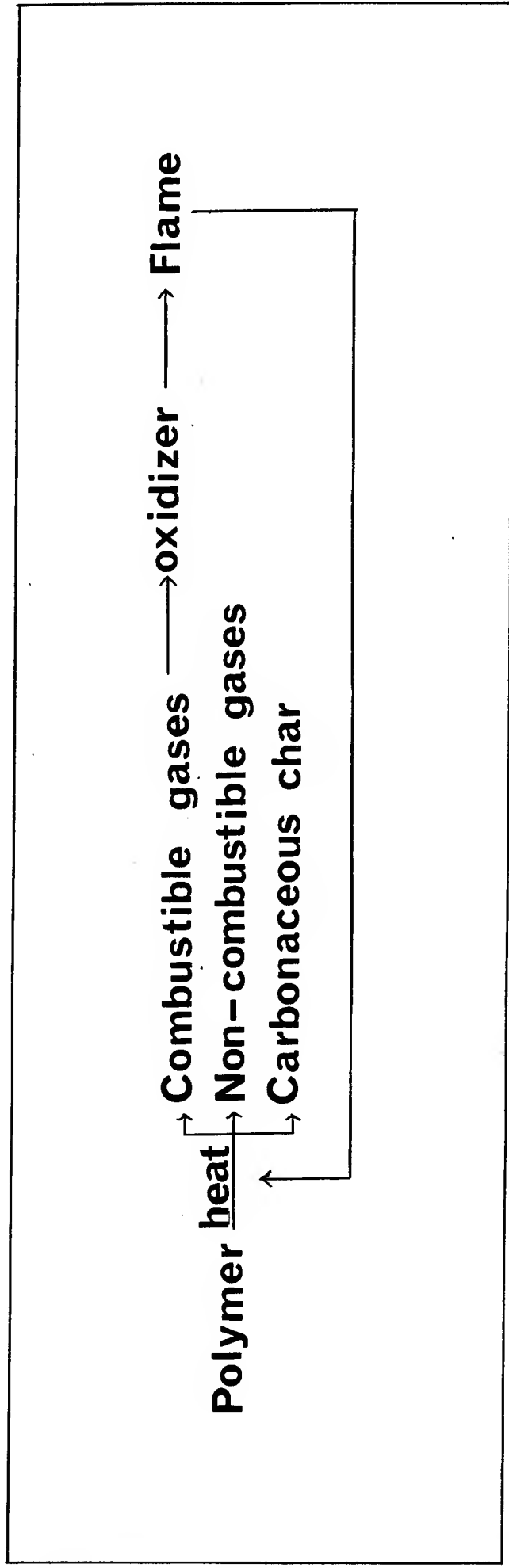


Fig. 1 Diagrammatic Representation of Polymer Burning Process

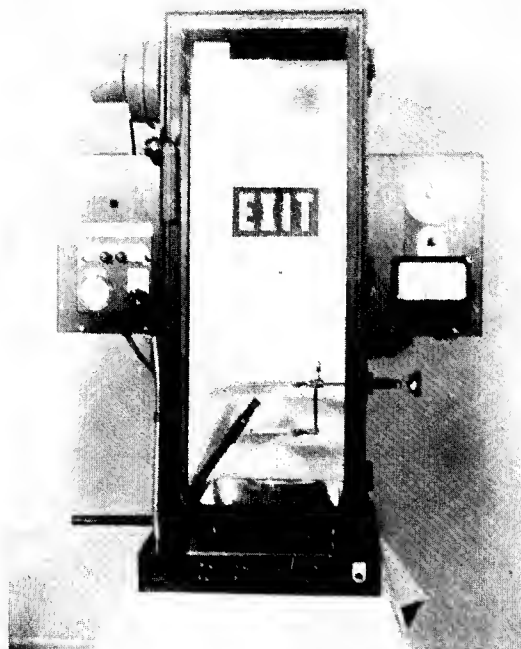
pendant to the polymer backbone to prevent chain scission during burning. Evolution of small unsaturated chain segments tend to form combustible gases during heating.

The incorporation of the elemental constituent into a chemically inert extender may permit migration of the non-reactive additive to the surface of the polymer where they may be lost in time. In addition, the non-reactive flame retardants act as diluents for the polymer and may lower the melting point or reduce dimensional stability.

The effect of crosslink density is of prime importance in raising the melting or decomposition point of the polymer. A highly crosslinked polymer will aid in char formation, resulting in a lower flame propagation. A low crosslinked polymer will tend to melt and drip during fire exposure. A highly cross-linked polymer will produce copious amounts of smoke during burning, while a low crosslinked polymer usually burns with a clean flame which produces little smoke.

Experimental

The smoke development properties of urethane foams were studied using a modified smoke density chamber⁽¹²⁾ illustrated in Figure 2. This chamber measures 12" by 12" by 31" and is constructed of anodized aluminum with stainless steel fittings. The door is cast aluminum with an inset fire resistant plate glass panel to permit observation of the test specimens during burning. An "Exit" sign is built into the rear of the chamber to permit visual observation of smoke obscuration. The sign is illuminated from the back by means of two six watt fluorescent lamps.



**Fig.2 Laboratory Scale
Smoke Development Chamber**

A quantitative analysis of smoke density may be measured by use of a Weston barrier layer photocell incorporated in the walls of the chamber at the level of the exit sign. The photocell operates in a dual range from 0 to 100% obscuration and 90 to 100% obscuration. A Sola transformer regulates the voltage supplied to the photometer, the signal may be directed to a servorecorder which permits a printout of % light obscuration versus time.

A fan is provided for exhausting the chamber at the completion of the test. It is possible to collect the smoke particles and effluent gases for analysis during or after burning.

Sample Preparation

Rigid and flexible urethane foams were prepared using prepolymer, quasi-prepolymer, and "one-shot" formulations. All specimens were machine poured utilizing a three component positive displacement mixing machine and a variable speed mixing head.

Specimens were subjected to a three hour postcure at 200°F to insure completion of the foaming reaction. The samples were stored at 70°F and 50% relative humidity for a period of fourteen days prior to evaluation.

Flexible Foam

A series of flexible polyether foams based on a propylene oxide adduct of glycerine (approximately 3000 M.W.) and toluene diisocyanate were prepared via the "one-shot" technique. Expansion was accomplished by the addition of water leading to the generation of carbon dioxide during processing. The idealized structure representing this foam is shown in Figure 3.

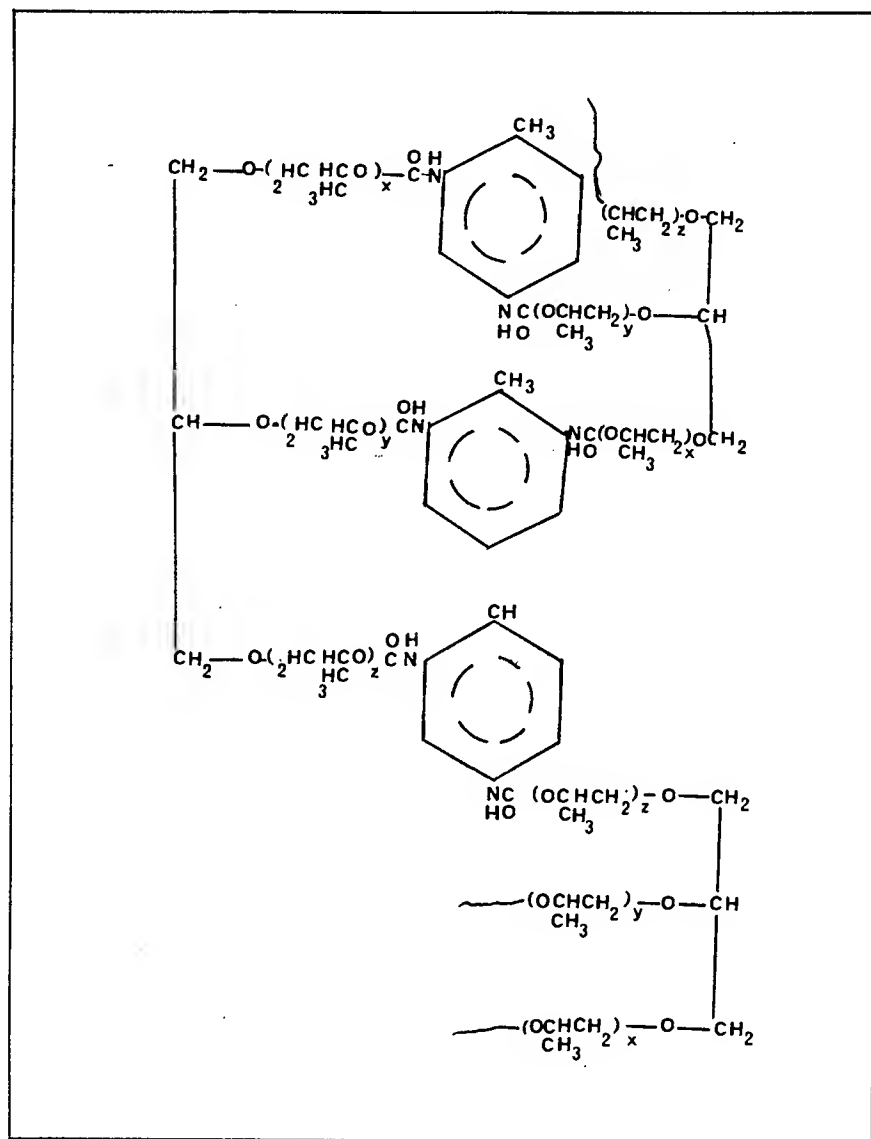


Fig.3 Idealized Structure for a Flexible Foam

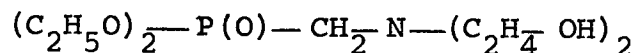
The basic formulation used to produce this series of foam samples is given in Table 1.

Table I.

Flexible Foam Formulations and Properties

Raw Materials	Parts by Weight
Propylene oxide adduct of glycerine. (3000 M.W.)	100.0
Tolylene diisocyanate (80/20 isomer ratio)	46.0
Water	3.7
Stannous octoate	0.3
Triethylenediamine	0.7
N-ethylmorpholine	0.1
Silicone oil	1.3
NCO/OH index	1.04
Density, lb/cu.ft.	1.6
Tensile strength, p.s.i.	19
Elongation, %	285
Compression set, 70°C, 50% RH (22 hours)	2.0

This basic formulation was modified to produce samples of a flexible foam extended (5% by weight) with a purified, finely ground form of the barium sulfate mineral barite. A fire-retardant flexible urethane foam was prepared by adding the reactive phosphorous containing polyol O, O-diethyl-n, n-bis (2-hydroxyethyl) aminomethylphosphonate:



The basic formulation was modified in order to maintain the desired stoichiometry.

Analysis of Flammability Characteristics of Flexible Foam Samples

Samples of the three foams prepared from the formulations described previously were burned in the smoke chamber. A summary of the observations made during the burning tests is presented in Table II.

The measured smoke obscuration rates obtained during the burning tests are summarized in Figure 4. The samples of foam prepared from the basic formulation burned readily and were consumed in twenty seconds. A small quantity of smoke was developed during the burning tests. Microscopic examination of collected particulate matter indicated that a rather uniform distribution of finely divided particles was deposited on the sample plates. Severe dripping occurred during combustion igniting cotton waste placed under the sample support.

Incorporation of an inert, non-reactive extender substantially reduced the burning rate, led to the reduction of smoke development during combustion, and minimized dripping.

Table II

Flammability Characteristics of Flexible Urethane Foam

<u>Sample Description</u>	<u>Density (p.c.f.)</u>	<u>% Light Obscuration</u>	<u>Time- Total Consumption</u>	<u>Remarks</u>
Basic Formulation	1.6	33	20 seconds	heavy drips
Barytes-Extended Foam	2.1	15	55 seconds	no drips
Fire Retarded Foam	2.0	65	40 seconds	moderate drips

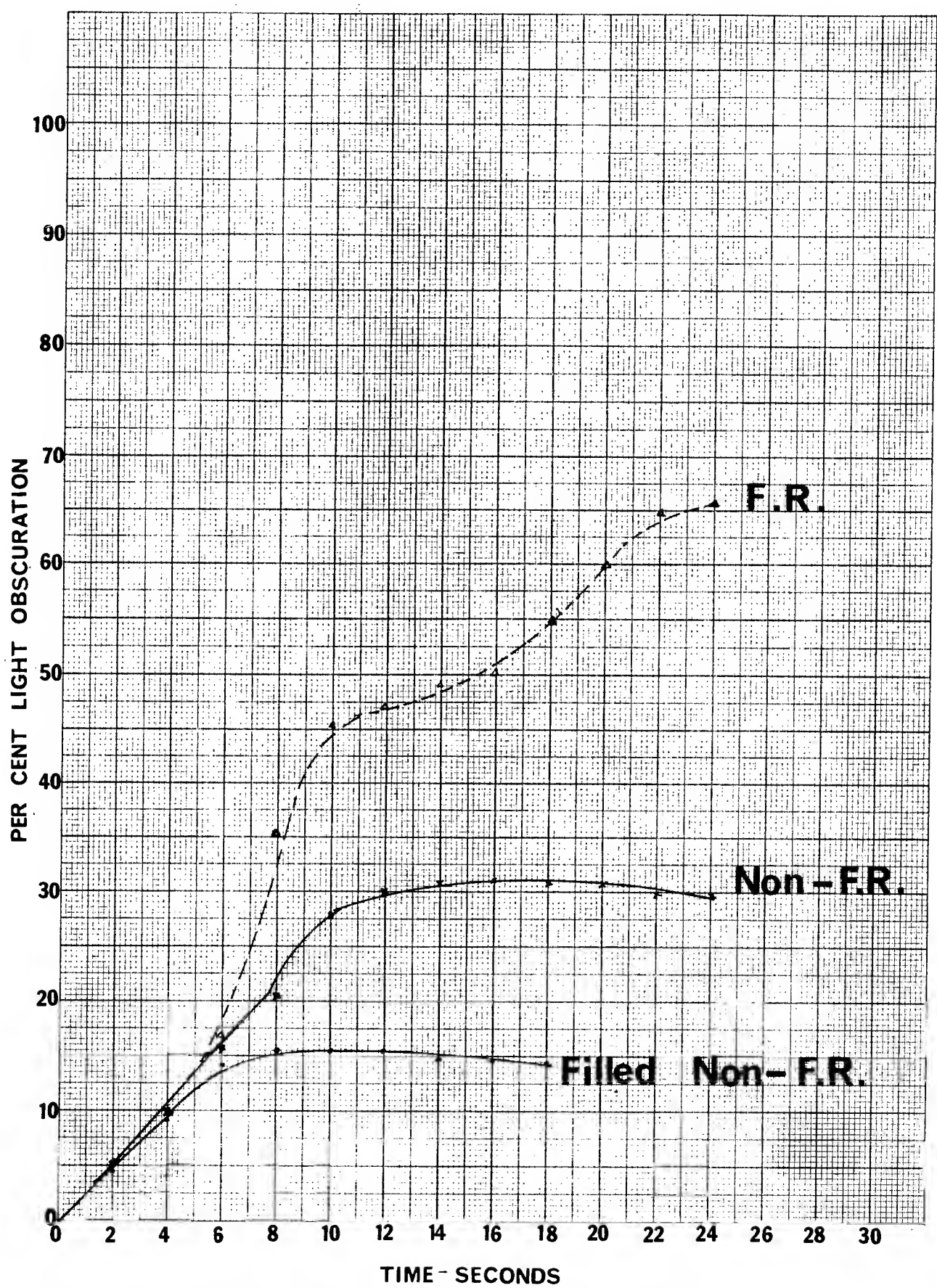


Fig. 4 Smoke Development in Flexible Urethane Foams

The addition of phosphorous (1.5% by weight) in the form of a reactive phosphonate fire retardant reduced the flame propagation rate as compared to the basis formulation. This addition of fire retardant led to an incomplete combustion process resulting in a doubling of the light obscuration rate.

Rigid Foams

A series of rigid urethane foams were prepared to illustrate the relationships that exist between chemical structure and flammability characteristics.

Effect of Isocyanate Structure

Urethane foams based on the propylene oxide adduct of sucrose, O, O-diethyl-n,n'-bis (2-hydroxyethyl) aminoethyl-phosphonate were reacted with tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, and polymethylene polyphenyl-isocyanate. Trichlorofluoromethane was the blowing agent used to expand these rigid foams. Figure 5 illustrates the idealized structure for a rigid urethane system based on tolylene diisocyanate, propoxylated sucrose polyol and a reactive phosphonate. Figure 6 shows the idealized structure for a rigid urethane foam system based on diphenyl methane 4,4' diisocyanate, propoxylated sucrose polyol, and a reactive phosphonate. Figure 7 presents an idealized structure for a rigid urethane foam system based on polymethylene polyphenyl-isocyanate, a propoxylated sucrose polyol, and a reactive phosphonate.

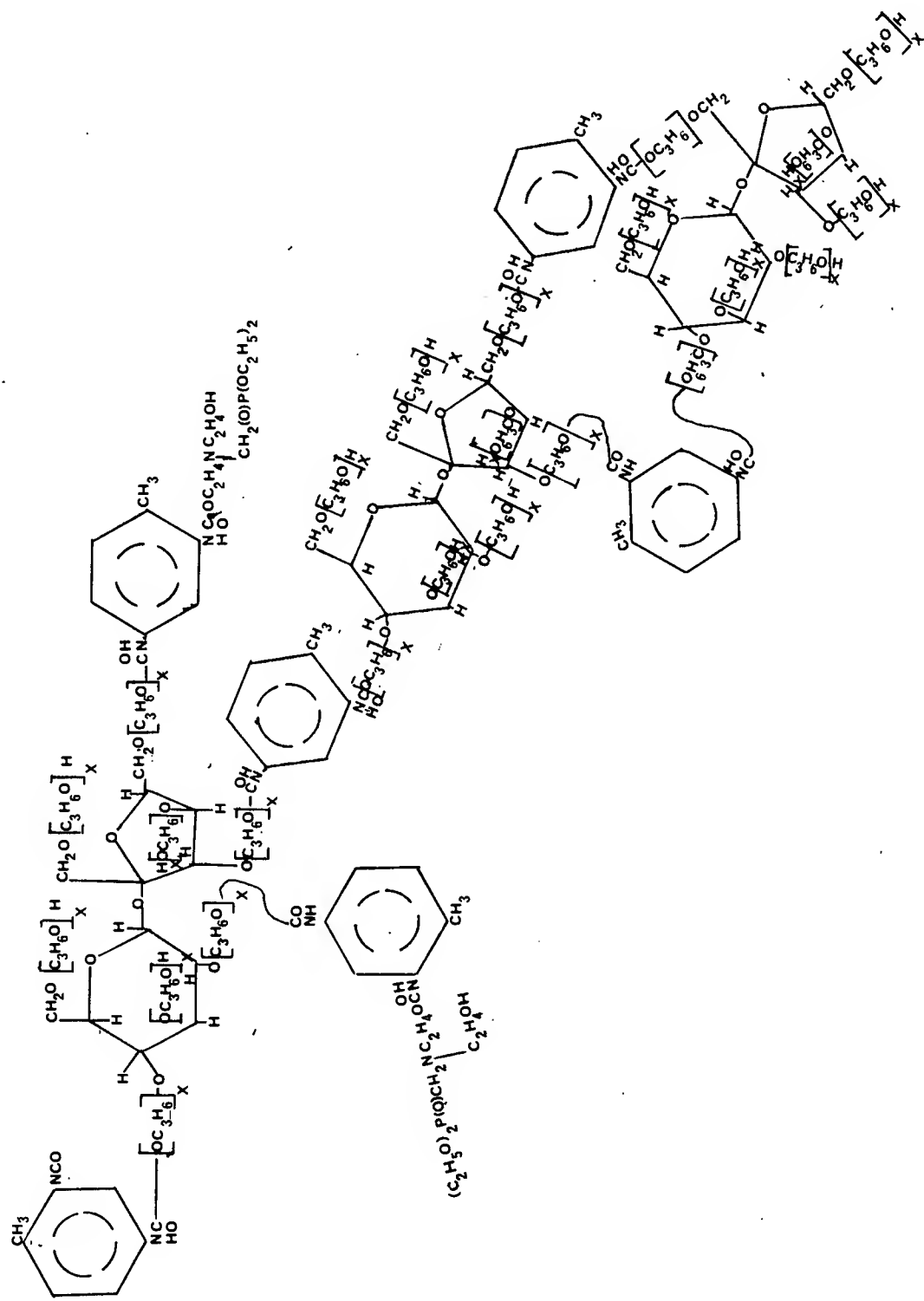


Fig.5 Idealized Structure for a Rigid Foam Based on Toluene Diisocyanate, Propoxylated Sucrose, and a Reactive Phosphonate

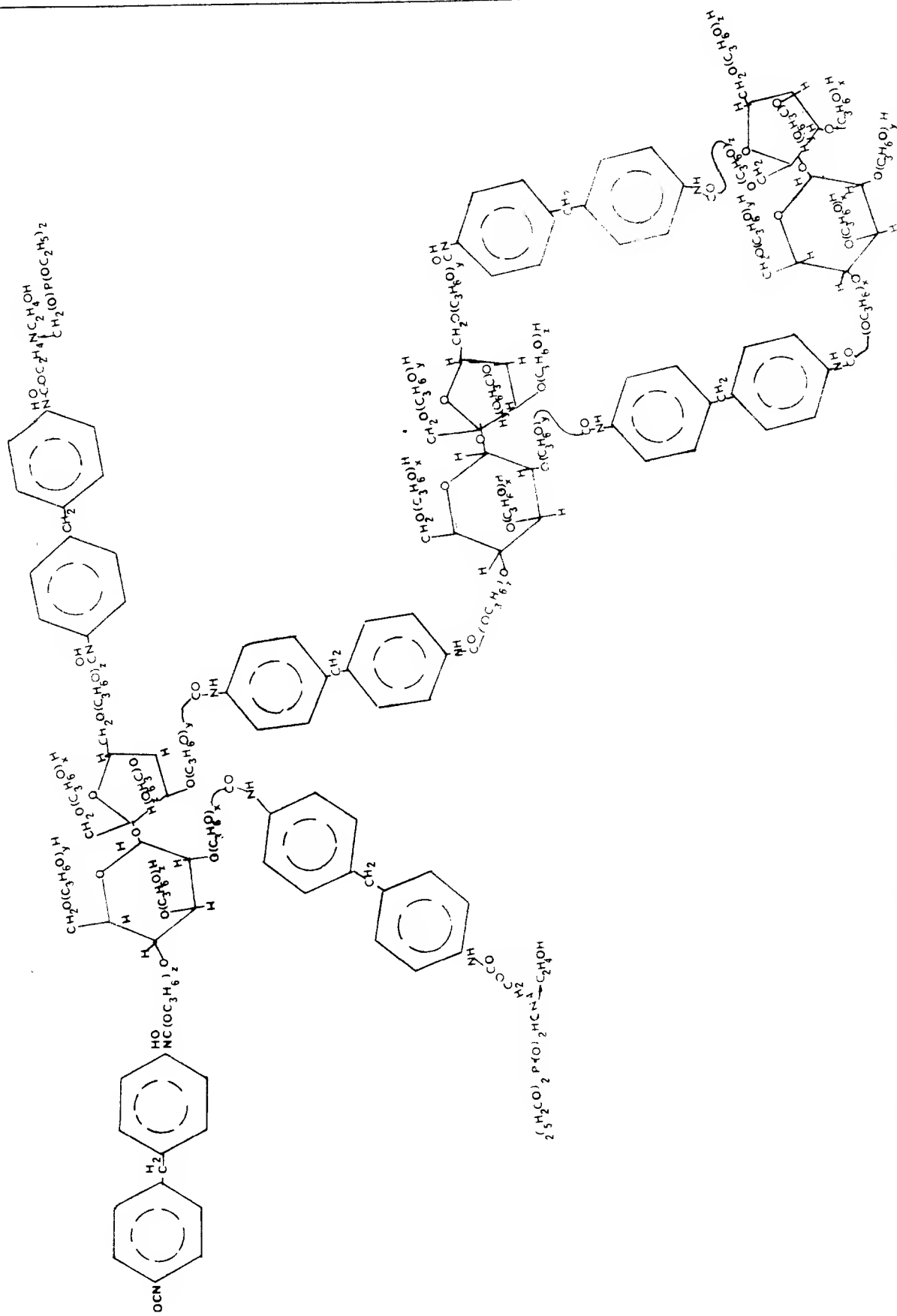


Fig.6 Idealized Structure for a Rigid Foam Based on Diphenylmethane 4,4'-Diisocyanate, Propoxylated Sucrose, and a Reactive Phosphonate

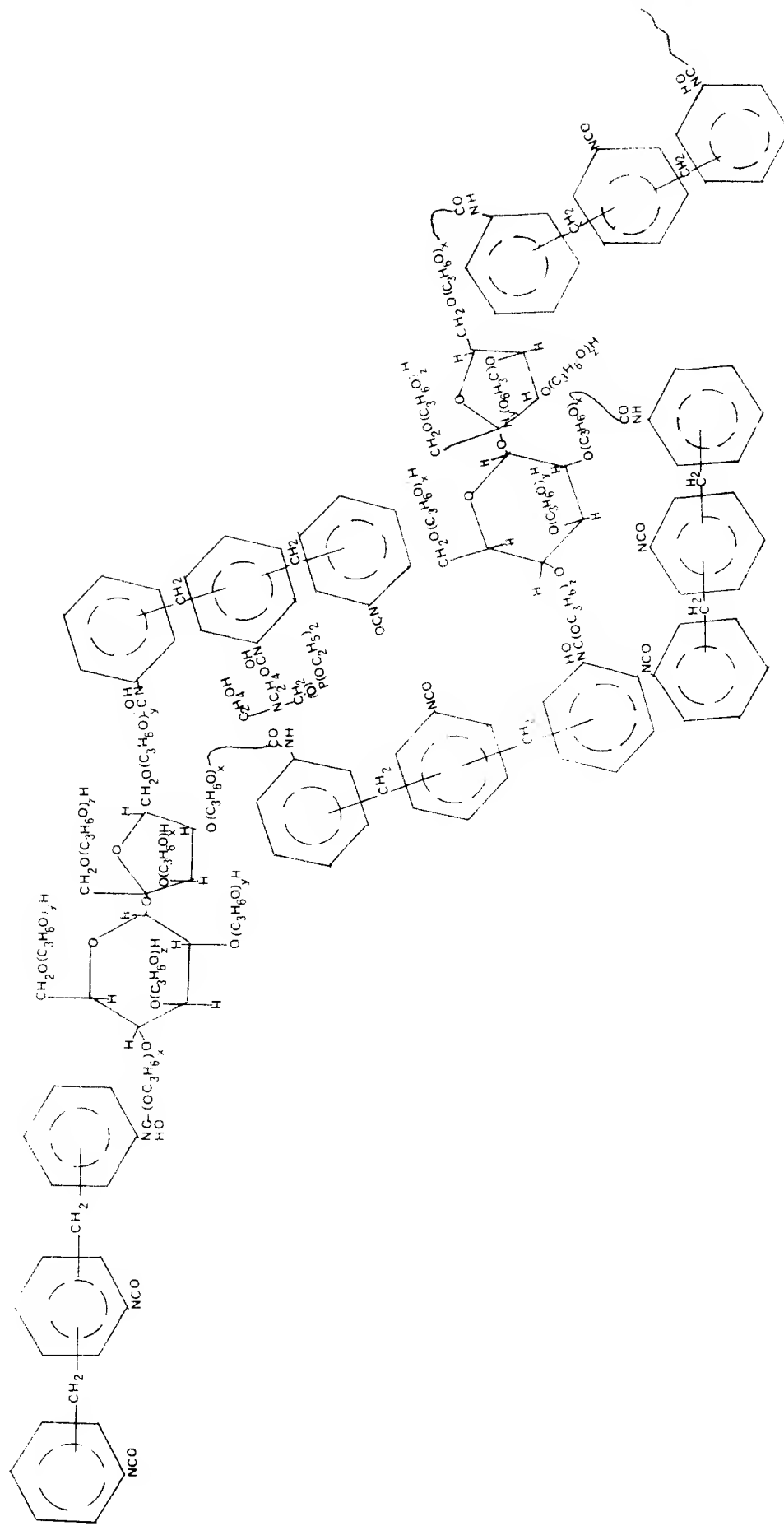


Fig. 7 Idealized Structure for a Rigid Foam Based on Polymethylene Polyphenylisocyanate, Propoxylated Sucrose, and a Reactive Phosphonate

The basic formulation used for the preparation of the rigid urethane foams described previously is given in Table III. Due to the high functionality and low equivalent weight of the propoxylated sucrose polyol, these foams were prepared by a modified quasi-prepolymer technique.

Initial burning tests indicated poor fire endurance characteristics for these foams, thus it was decided to replace the quasi-prepolymer system with a "one-shot" formulation. The halogen containing fire retardant was replaced by the reactive phosphonate shown in the idealized structures. The reactive fire retardant was added so as to incorporate 1.5% by weight of phosphorous in the final foam composition. Necessary adjustments were made to maintain the desired stoichiometry. The NCO/OH index was raised from 100 to 105 for the foam systems based on reactive phosphonate to facilitate greater stability during preparation.

Samples of the four rigid foam systems described previously were burned in the smoke chamber. A summary of observations made during the burning of test specimens is presented in Table IV. Analysis of data obtained during the combustion of urethane foams shows that as the degree of aromaticity within the urethane polymer is increased (isocyanate fraction) the fire endurance characteristics of the foam improves and the flame propagation rate decreases. It was observed that as the degree of fire retardancy improves, the rate of smoke development caused by incomplete combustion of the foam increases. Figure 8 compares the rate of smoke development (light obscuration) measured during the burning process.

Table III

<u>Component A</u>	<u>Parts by Weight</u>
Propoxylated sucrose polyol (OH no. 443)	127.0
Trichlorofluoromethane	40.5
Triethylenediamine	0.8
Silicone oil	0.8
Chlorinated diphenyl	Adjusted to produce desired chlorine content
<u>Component B</u>	
Quasi-prepolymer (29.4% excess NCO)	143.0
NCO/OH Index 100	
<u>Foam Physical Properties</u>	
Density, lbs./ft. ³	2.1
% Closed Cells	92
Compressive Strength (Yield at 20°F)	50
K-Factor (Initial)	0.112
Moisture Vapor Transmission, perm inches	3.5

Table IV

Flammability Characteristics of Rigid Urethane Foams

Sample Description	Density (p.c.f.)	% Light Obscuration	Obscuration Time-Seconds to:		% Weight Loss
			50%	100%	
Propoxylated sucrose-TDI, chlorinated diphenyl foam	2.1	42	---	---	100 (25 sec.)
Propoxylated sucrose-TDI, phosphonate foam	2.0	90	9.5	---	100 (40 sec.)
Propoxylated sucrose, diphenyl methane 4,4', diisocyanate foam	2.1	96	3.0	---	40
Propoxylated sucrose, polymethylene polyphenyl- isocyanate, phosphonate foam	2.1	100	1.0	4.0	26

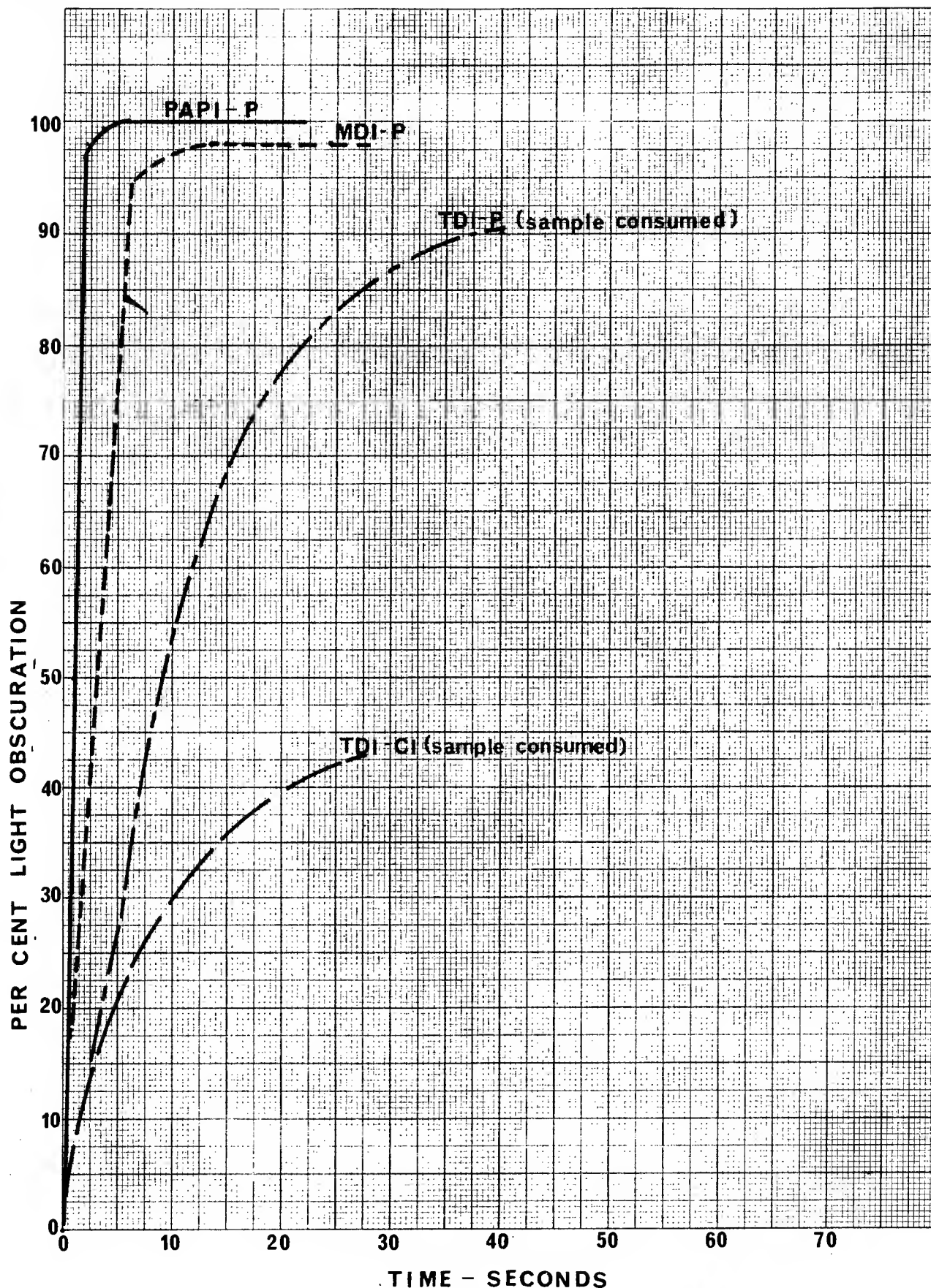


Fig.8 Relationship Between Isocyanate Structure and Light Obscuration

Specimens which were fire retarded with the chlorinated diphenyl did not develop a strong char structure, while those fire retarded with a reactive phosphonate did. These results are in agreement with the earlier reported studies of Mitchell.⁽¹³⁾ Table V shows the relationships that exist between the type of fire retardant and foam properties.

Effect of Fire Retardants

A series of rigid urethane foams were prepared varying the type of fire retardants incorporated into the formulation. Table VI summarizes the formulations used to prepare this test series.

The specimens were burned in the smoke chamber and the results recorded by photographic techniques. The control sample (3079-10) which did not have a fire retardant incorporated into the polymer structure had the lowest rate of smoke development. This specimen exhibited strong char formation and lost approximately 25% of its initial weight during the combustion period. Total light obscuration occurred at 30 seconds after ignition. The specimen (3079-13) which contained a phosphorous and chlorine fire retardant showed the highest degree of smoke development of all samples tested in this series. A moderately strong char formed during the combustion period. Approximately 70% weight loss occurred during burning. A secondary explosion, which was attributed to ignition of unsaturated short chain segments of the polymer, occurred 18 seconds after ignition. Total light obscuration occurred 9 seconds after ignition. The two specimens, (3079-18; 3079-32) utilizing a phosphorous containing polyol incorporated into the polymer to impart fire retardancy

Table V

Effect of Phosphorous and Chlorine Inhibitors on the Auto-Ignition
Temperature and Char Strength of Urethane Foam

<u>Inhibitor</u>		<u>Auto-Ignition Of</u>	<u>Char Strength</u>
<u>Phosphorous Content %</u>	<u>Chlorine Content %</u>		
0	0	950	None
0	50	950	None
5	50	1,000	Weak
10	0	1,150	Strong

(Ref. 13)

* Foams made from diphenyl methane 4,4' diisocyanate, propoxylated sucrose polyol (OH #460) and CCl_3F blowing agent.

Table VI

Basic Formulations for Rigid Urethane Foams
Fire Retardant Study

Reactants	Test Specimens				
	Control 3079-10	3079-13	3079-18	3079-32	
Propylene oxide adduct of sorbitol (OH #490)	83.4	83.4	56.0	55.0	
Trichlorofluoromethane	28.0	40.0	28.0	27.0	
Silicone Surfactant	1.0	1.0	1.0	1.0	
Triethylenediamine	0.15	0.15	0.2	0.08	
N, N-Dimethylethanolamine	1.2	1.2	1.2	1.2	
Polymethylene polyphenylisocyanate	100.0	100.0	100.0	83.0	
$ \begin{array}{c} \text{H}_2\text{H}_2\text{O} \quad \text{H} \quad \text{O} \\ \text{ClC}-\text{C}-\text{O}-\text{P}-\text{O}-\text{C}-\text{P}-\text{O}-\text{C}-\text{P}(\text{OCHCHCl}) \\ \text{Cl} \quad \text{C} \quad \text{CH}_3 \quad \text{OCH}_2\text{CH}_2\text{Cl} \\ \text{H}_2\text{H}_2 \end{array} $	---	31.0	---	---	*
$ \begin{array}{c} \text{O} \\ \parallel \\ (\text{C}_2\text{H}_5\text{O})_2\text{P}-\text{CH}_2\text{N}(\text{C}_2\text{H}_5\text{OH})_2 \end{array} $	---	---	31.0	---	**
Phosphorous Containing Polyol (OH #212) ***	---	---	---	30.0	
Foam Density, p.c.f.					

* Phosgard C-22R, Monsanto Chemical Company

** Pyrol 6, Victor Chemical Division, Stauffer Chemical Company

*** Vircol-82, Mobil Chemical Company

characteristics exhibited similar rates of smoke development. Sample 3079-18 retained 45% of its initial weight after combustion. Total light obscuration occurred 15 seconds after ignition. Sample 3079-32 retained 43% of its original weight after combustion. Total light obscuration occurred 16 seconds after ignition. Figure 9 illustrates the rate of light obscuration measured for each of the test specimens.

Thermal gravimetric analysis studies were carried out on the test specimens using a du Pont 940 TGA unit coupled to the 900 DTA chasis. The related thermograms are shown in Figure 10. The specimen containing the chlorine and phosphorous fire retardants (3079-13) showed slightly higher weight retention than the other samples after being subjected to 500°C temperature programmed at a rate of increase of 10°C per minute.

Differential thermal analysis studies of the test specimens were carried out using the du Pont 900 DTA unit. Examination of the thermograms obtained after heating the specimens at a rate of 10°C increase per minute (Figure 11) showed that degradation occurs at approximately 300°C (in good agreement with TGA studies). The control specimen showed a modest exotherm following decomposition. The development of a second exotherm after the onset of thermal decomposition is typical of many foams not utilizing a built-in fire retardant. The fire retarded samples show strong endotherms following thermal decomposition. This endotherm is seen in samples which have high rates of smoke development.

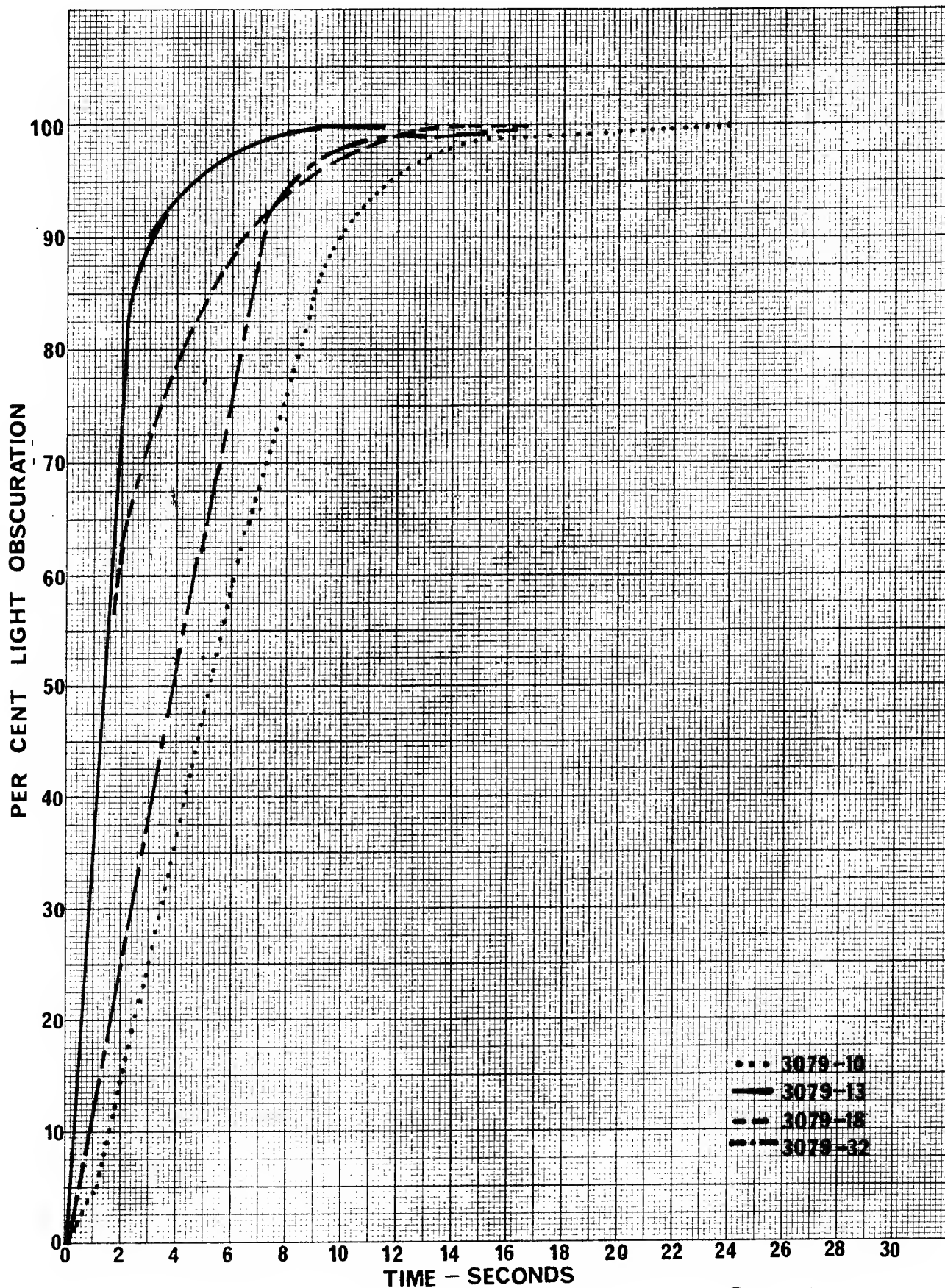


Fig. 9 Effect of Fire Retardant on Smoke Development

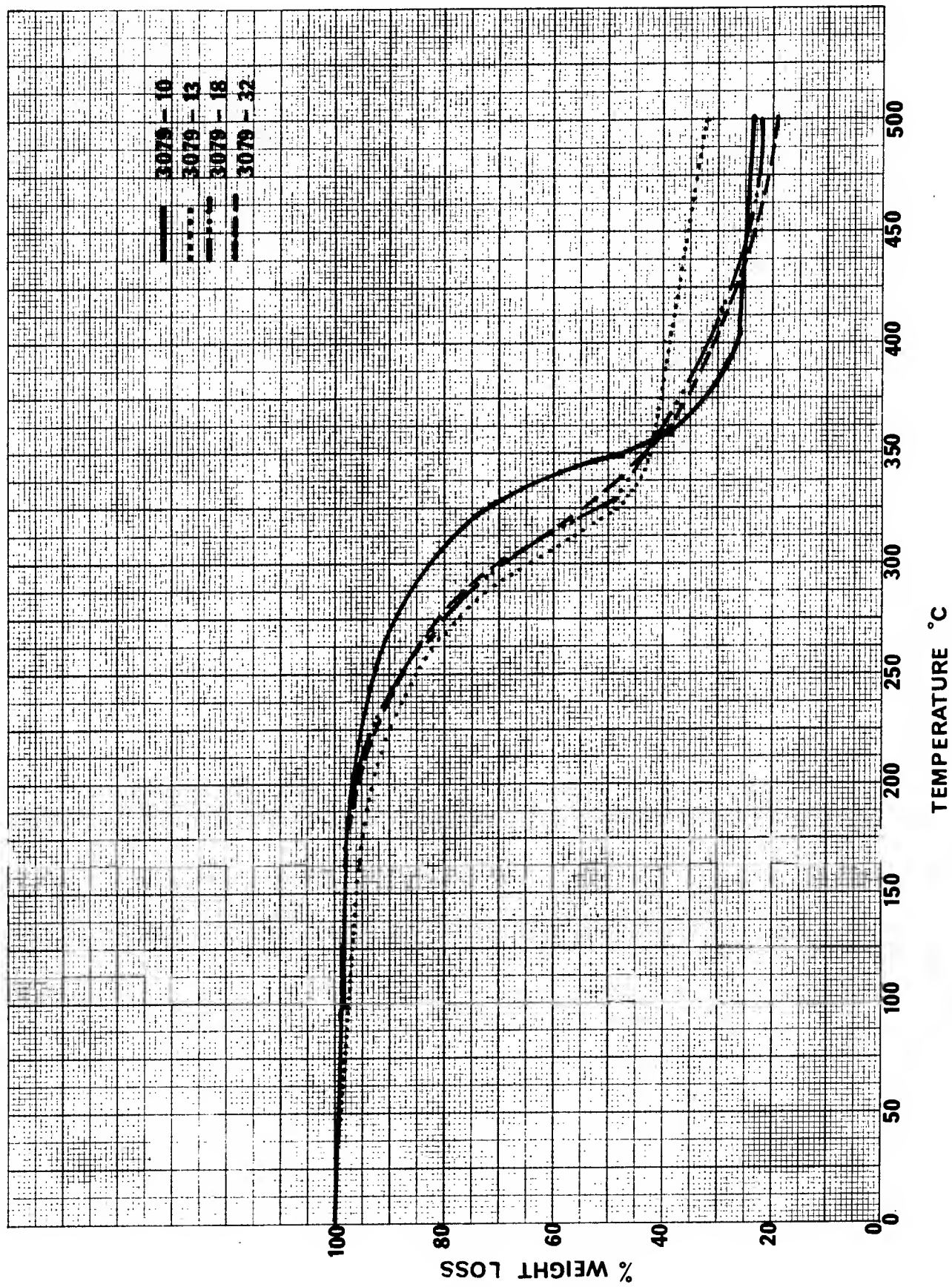


Fig.10 Effect of Fire Retardant on Foam Degradation (T.G.A.)

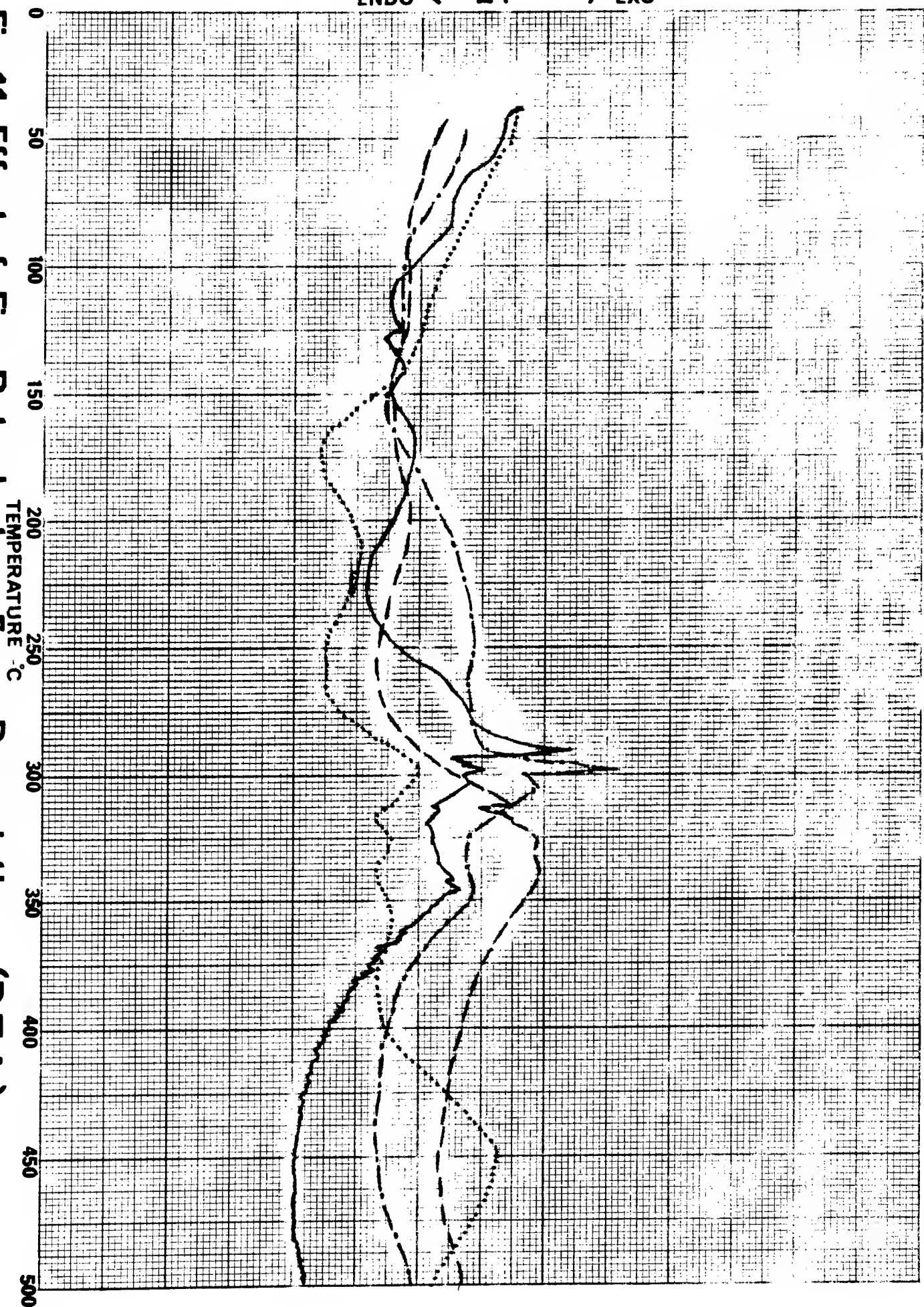
ENDO ← ΔT → EXO

Fig. 11 Effect of Fire Retardant on Foam Degradation (D.T.A.)

Effect of Polyol

Initial exploratory experiments were undertaken to determine the effect of polyol structure on the flammability characteristics of rigid urethane foams. Observations made during the combustion of test specimens in the smoke chamber indicated that a more detailed, statistically designed experiment would be necessary to evaluate the effect of interactions involved in smoke development. Figure 12 illustrates the results observed during the initial burning test. Formulations utilizing highly aromatic polyols (or isocyanates) will produce copious amounts of smoke during burning. The addition of a fire retardant which aids in char formation will substantially increase the rate of smoke development. Formulations which are not based on highly aromatic polyols (or isocyanates) result in more complete combustion during exposure to a flame source and produce less smoke.

Effect of Cross-Link Density, Mc

Anderson⁽¹⁴⁾ has reported on the relationship between the average molecular weight per cross-link and the flammability characteristics of urethane foams. A series of foam samples were prepared using polymethylene polyphenylisocyanate, propoxylated sorbitol, and trichlorfluormethane as the major components. The sorbitol used in this experiment was propoxylated in the laboratory to a varying range of molecular weights. The fluorocarbon content was determined experimentally in order to produce samples of equal density.

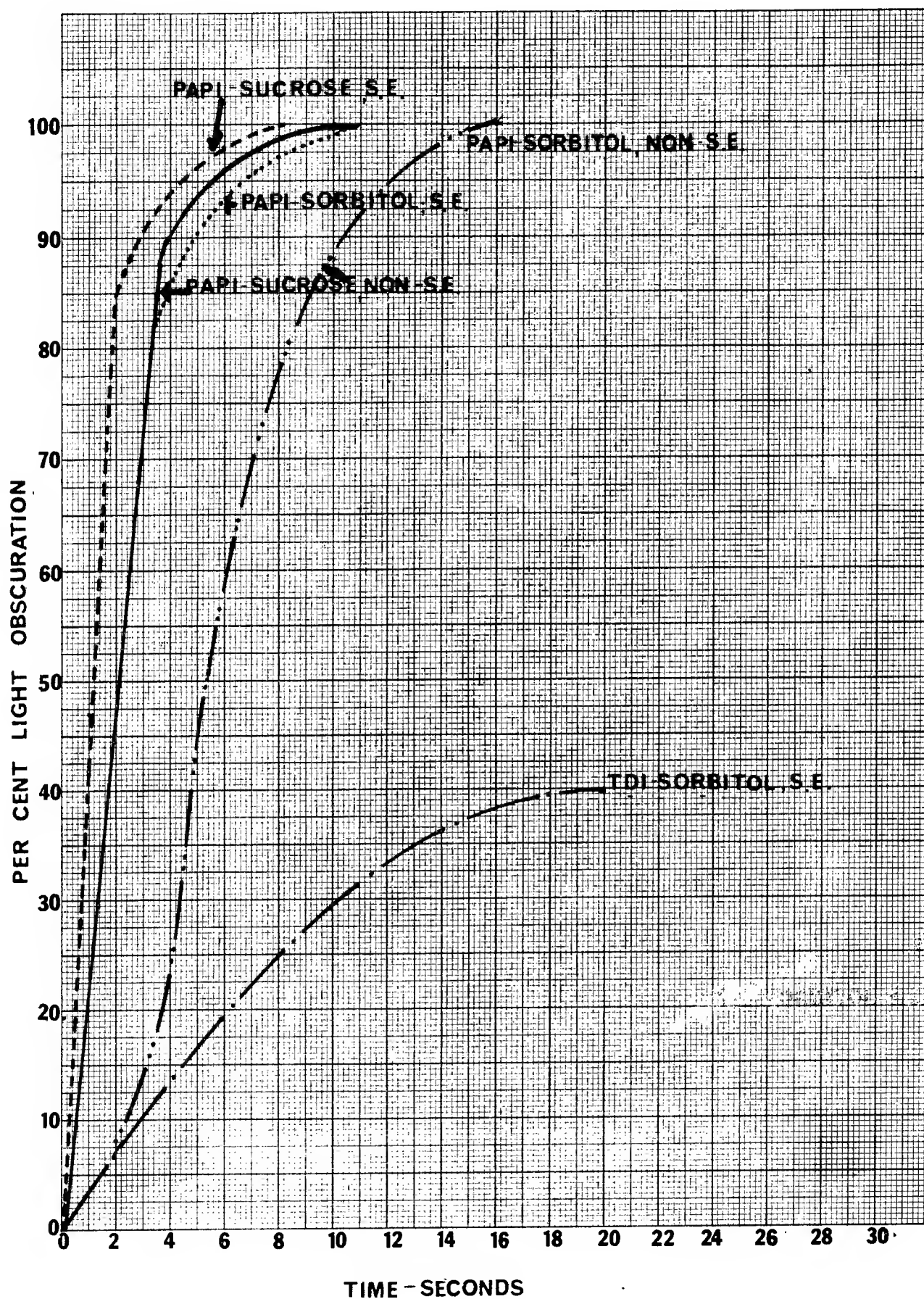


Fig.12 Effect of Polyol Structure on Smoke Development

Samples varying in molecular weight from approximately 230 to 560 were evaluated in the smoke chamber. A direct relationship was observed between the molecular weight per cross-link and smoke development. Figure 13 presents the family of curves developed as results of combustion of the test specimens in the smoke chamber. Samples prepared having a Mc ranging from 230 to 290 formed a strong char when exposed to a flame source. The foam specimens having an Mc of 320 developed a weak char and exhibited moderate distortion when burned. The sample having an Mc of 415 formed a weak intermittent char and moderate intumescence structure during burning. The sample having an Mc of 540 was extinguished after 25 seconds; this sample melted slowly away from the flame source and would have been entirely consumed.

Effect of Density

Initial exploratory experiments have been carried out to determine the effect of foam density on the smoke development and burning characteristics of cellular plastics. Table VII shows the formulations used to produce foams of varied density.

Figure 14 shows the family of curves developed during combustion of the test specimens in the smoke chamber. All samples generated approximately the same degree of smoke during combustion. Additional experiments are being conducted to verify these results.

A review of thermograms indicates good correlation between initial fluoro-carbon content and sample weight loss during heating. (Figure 15)

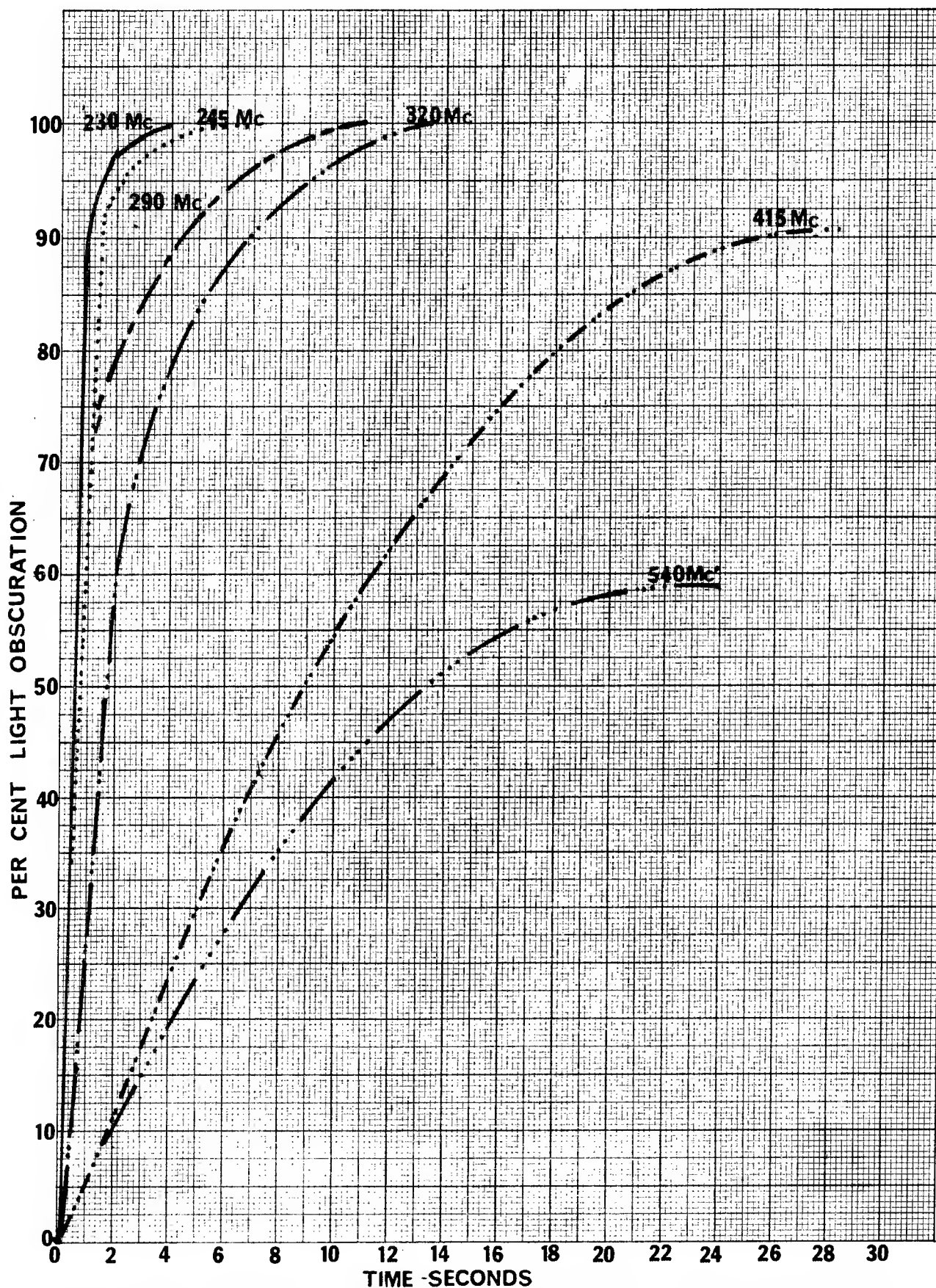


Fig.13 Effect of Mc on Smoke Development

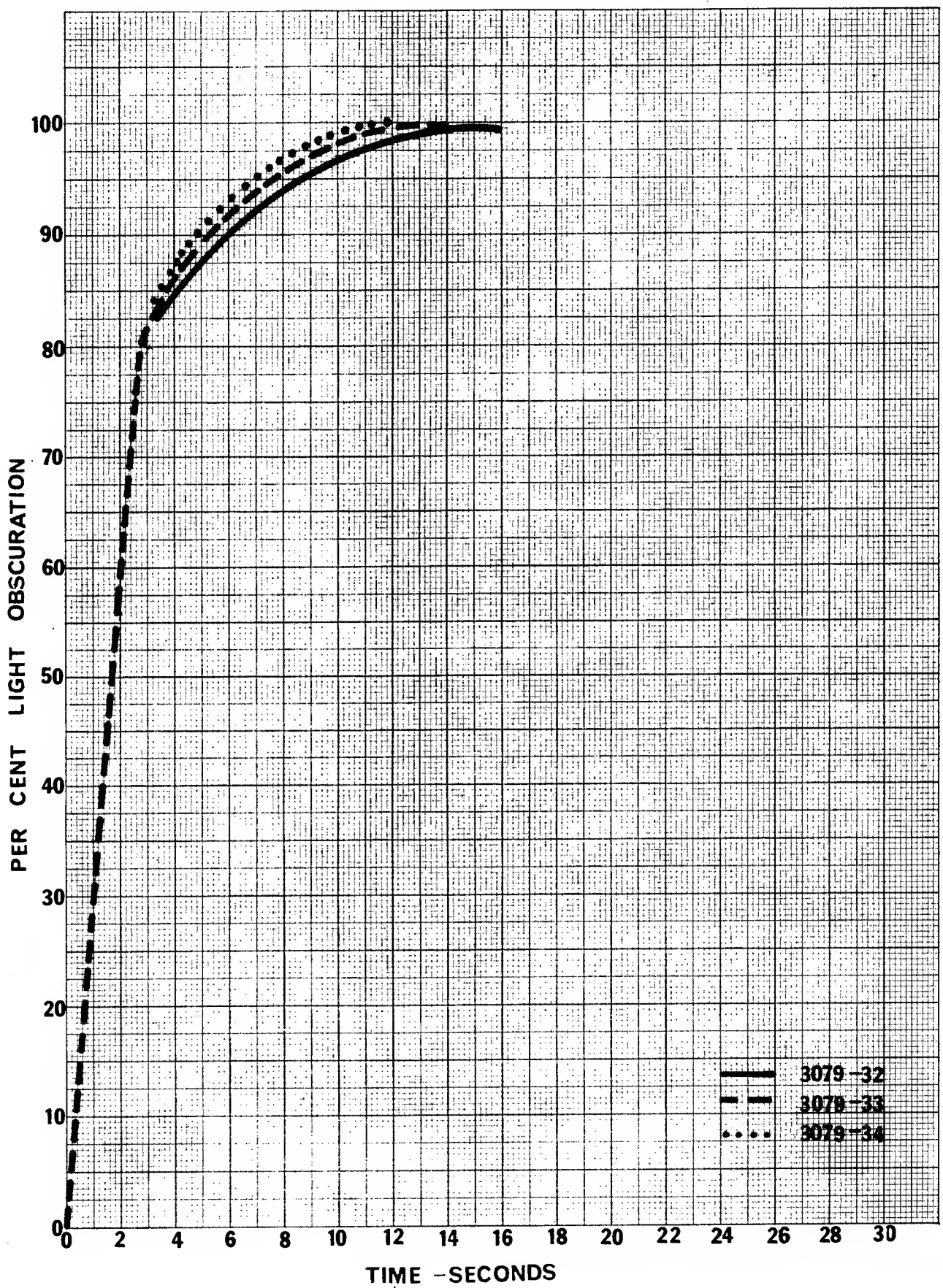
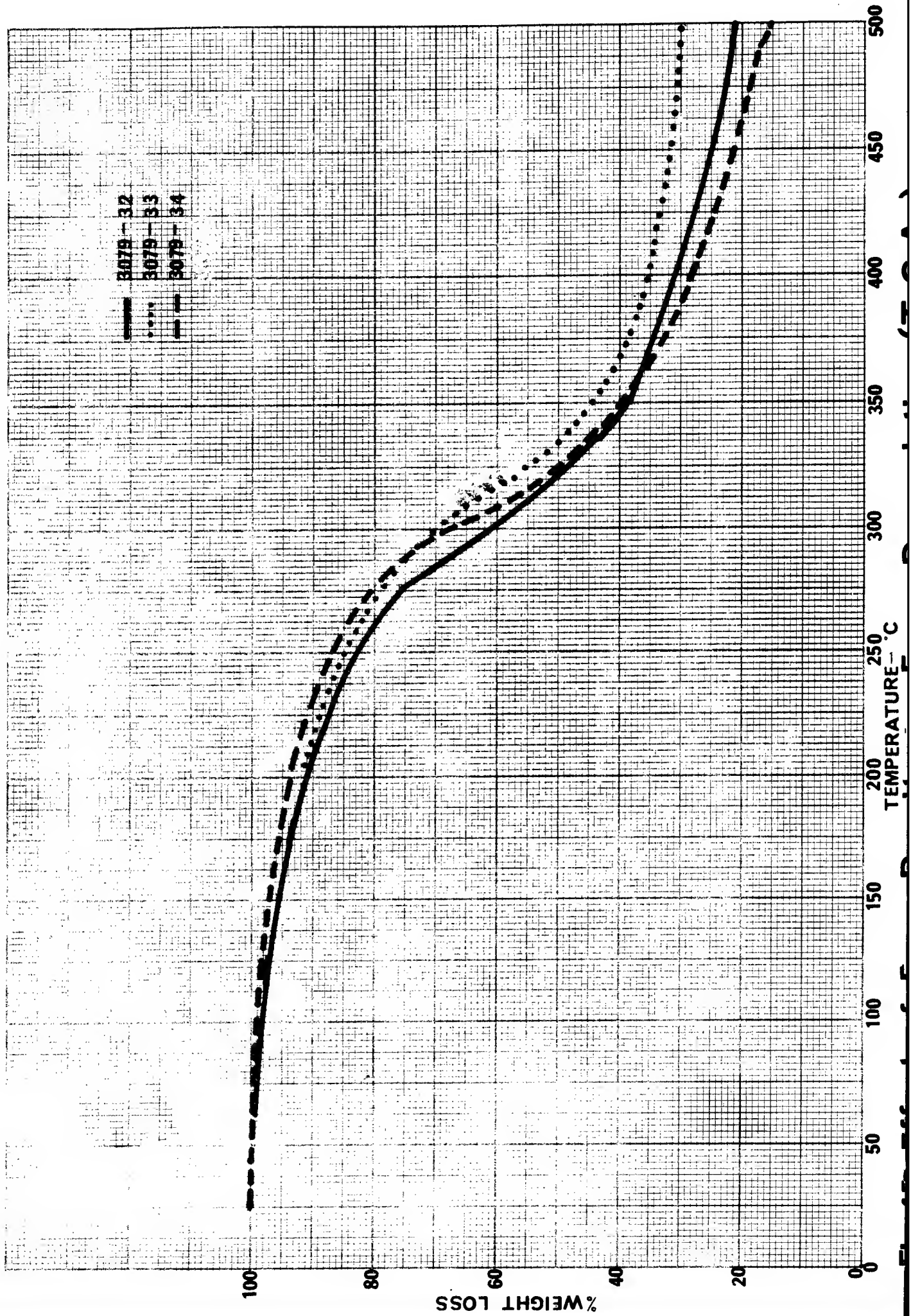


Fig.14 Effect of Density on Smoke Development



Summary and Conclusions

A research program established by the State of Michigan has been conducted by the Department of Chemical Engineering of Wayne State University to study the flammability characteristics of polymeric materials. This report summarizes the results of a program designed to study the parameters relating to smoke development in urethane foams.

A series of flexible and rigid urethane foams have been designed, prepared, and evaluated in the laboratory. Good correlation exists between factors governing the generation of smoke during combustion under laboratory conditions and those reported in large scale industrial fires.

Evaluation of the data obtained in numerous experiments strongly indicates that the development of foam systems which develop char structure during combustion either by design of high cross-linked chemical structure or the incorporation of flame retardants produce considerable quantities of dense smoke. Analysis of pyrolytic degradation products produced during combustion of rigid urethane foams under laboratory conditions may, in a large scale fire, present a serious hazard to occupants of structures as well as those individuals seeking to control the conflagration.

A review of actual case histories reported in the literature and numerous private communications with scientists and engineers engaged in the study of large fires has clearly indicated that the rapid development of large quantities of smoke and toxic decomposition products during combustion, is the greatest single factor resulting in loss of life or bodily injury during fires occurring in buildings. Present regulatory

practices stress the desirability of reducing the flame propagation of materials of combustion while paying little attention to smoke development or generation of toxic products. This policy has resulted in the development of "fire-retardant" plastics designed to meet code acceptance. In reality, many of the materials presently specified as meeting these unrealistic codes actually present a far more serious hazard during fire exposure than those "non-fire retarded" materials which, in fact, cannot be specified due to their inability to meet existing requirements pertaining only to flame propagation.

It is the opinion of the author that the data developed during the course of research reported on in this paper illustrates the conclusions drawn above. We therefore urge that immediate consideration be given to the development and specification of polymeric materials which while possessing reasonably low rates of flame propagation, do not contribute to potential hazards during combustion.

Further research in being directed toward the understanding of the mechanism and kinetics of combustion of foamed plastics in an effort to establish an understanding of principles which will permit the development of cellular plastics which will respond to fire exposure with reduced hazards.

Acknowledgements

The authors wish to acknowledge their gratitude to the Michigan Legislature and the Michigan Department of Economic Expansion for providing the funds and other support which enabled us to undertake this research project.

We further wish to acknowledge the contributions made by Professors S. Stynes, Department of Chemical Engineering, and H. K. Livingston, Department of Chemistry, for their continued advice and consultation during the past year.

Finally, we wish to acknowledge the assistance of Mr. R. Craig who assisted in testing many of the materials reported on during the scope of this paper.

Bibliography

1. Buck, G. S., Jr., "Fire Resistant Textiles," Kirk-Othmer Encyclopedia of Chemical Technology, Wiley, Vol. 6, 543 (1951).
2. Saunders, J. H. and Backus, J. K., "Thermal Degradation and Flammability Characteristics of Urethane Polymers," Proceedings, Wayne State University Polymer Conference, May, 1965.
3. Dickert, E. A., and Toone, G. C., S.P.E. Antec Proceedings, May 7, 1964.
4. Ibid.
5. Ibid.
6. Ibid.
7. Eichhorn, J., A.C.S., Div. Org. Coatings and Plastic, Papers 23, No. 1, p. 37 (1963).
8. Boyer, H. E., Plastics Tech. 8, No. 11, 33 (Nov. 1962).
9. Nametz, R. C., Deanin, R. D. and Lambert, P.M., A.C.S. Div. Org. Coatings and Plastics Chem., Papers, 23, No. 1, p. 126 (1963).
10. Jahn, A. J., and Vanderhoff, J. W., A.C.S., Div. Org. Coatings and Plastics Chem., Papers, 23, No. 1, p. 61(1963).
11. Piechota, H., J. Cel Plastics, Vol. 1, No. 1 (Jan, 1965).
12. Private Communication, Roam and Haas Company, Philadelphia, Pa.
13. Mitchell, D., "Correlations Between Samll Scale and Full Scale Fire Tests," Proceedings Wayne State University Polymer Conference, June, 1966.
14. Anderson, J. J., "The Relationship of Crosslinked Density to the Flammability Characteristics of Polyurethane Foams," Proceedings Wayne State University Polymer Conference, June 1966.

1 0214-09
29661

POLYETHYLENE FOAM III -
"ORIENTATION IN THERMOPLASTIC FOAMS"

BY

Dr. Calvin J. Benning

W. R. GRACE & COMPANY
WASHINGTON RESEARCH CENTER
JUNE, 1966

POLYETHYLENE FOAM III -
"ORIENTATION IN THERMOPLASTIC FOAMS"

INTRODUCTION

This paper describes the expansion of thermoplastics, (for example, low density polyethylene, linear and high density polyethylene and polystyrene) in terms of film orientation. This is the first attempt to use film orientation techniques to describe the expansion of polymers.

Our basic reasoning can be summarized as follows:

A low density unicellular foam consists of an infinite series of cells or membranes. These membranes have been produced by resin expansion at high rates of strain. If one examines the expansion process and microscopically analyzes the foam structure, certain similarities to film orientation become apparent. For example, the cell windows of foams expanded at moderate rates have the appearance of miniature oriented films. In fact, the behavior of an isolated cell membrane on a hot stage microscope (heated slowly to the m.p. of the resin) resembles that of a shrink film. The membrane appears to shrivel and contract before it reaches the m.p., this indicated a certain degree of orientation.

The immediate question one has to answer, therefore, is "Are foams constructed of oriented films joined by heavy junctions"? If the foams contain oriented cells then one should expect to obtain a correlation between the orientation behavior of films and the expansion of the resin. Or one should note a dependance of mechanical properties on the rate of expansion.

If foam cells are not oriented, in the true sense of the word, but are partially relaxed, then the next question to be answered is "How does one produce an oriented cell structure and reduce stress relaxation in the foam." This is needed to produce high strength composites. Perhaps one would hope to control the relaxation by the proper choice of resin, blowing agent or process.

In our studies we have discovered several interesting phenomenon that operate in both film orientation and thermoplastic expansion.

In the following sections of this paper we will discuss:

1. Our apparatus and techniques.
2. The orientation of free blown films, and how their behavior relates to the expansion process.
3. The properties of thermoplastic foams prepared at different rates of expansion and of oriented films prepared at the same rate.
4. The analysis of foams to determine the degree of orientation, and finally.
5. We will describe a hypothetical system that one may expect to yield a high strength composite.

EXPERIMENTAL

1. Film Apparatus

A modified "free blown film" apparatus was used to study the orientation process and prepare oriented films. The apparatus is illustrated in Figure 1 and has been described in the literature.^(1,2)

Films and molded plaques were clamped into the form and heated to the desired temperature with radiant heaters. A thermocouple recorded the temperature of the film. At a pre-determined temperature the heater is removed and the film is expanded. Pressure regulating devices, micro-switches, etc. were the usual auxiliary equipment.

A typical sample of 4" x 4" x .020" PE cross-linked to 60% gel with organic peroxide was expanded to a 2000 to 4000 cc sphere in less than two seconds.

Provisions for a pressure recorder could be attached to the apparatus to record the stress-strain behavior during expansion. Behavior of films during these high speed stress-strain tests can be expected to correlate with high speed expansion of bulk polymers.

The area under the stress-strain curve is proportional to the energy required to rupture the material and if the "free blown film" test is made at a high enough rate, the area under the curve should be the same as the impact strength of the film. The impact strength in turn is related to the tensile strength and elongation at failure, or maximum extensibility of the resin during expansion. The tensile increases and the elongation decreases with an increase in orientation.

The amount of film orientation was calculated by dividing the surface area of the sphere by the area of the unstretched molded film.

2. Foam Preparation

The polyethylene foams were prepared by conventional techniques and have been described previously, for example:

Linear polyethylene foams were prepared at high rates of expansion 2000%/<2 seconds by a compression molding process described in reference 3, 4 and 5 in the Bibliography. Linear polyethylene foams prepared at medium and low rates of expansion have been described previously by us.⁽⁶⁾

Low density polyethylene foams were also prepared by the compression molding process using an exothermic blowing agent (azobisformamide) at high rates of expansion (2000%/<2 seconds) and by an extrusion foaming process using Freon or 4,4' oxybis (benzene sulfonyl hydrazide) described in the literature^(4,7).

Polystyrene foams were prepared from the foamable beads by pressure expansion (slow rate of expansion) and the conventional extrusion expansion (fast rate). Both methods were investigated using the same resin with the pentane blowing agent. Extreme care was used to produce uniform foams having similar cell structure.

3. Orientation in Films and Foams

We have analysed polyolefin foamed structures and they have the appearance of a multitude of biaxially oriented (inflated) spheres crowded together in a minimum volume to yield a modified polyhedron with spherical segments. If our analysis is reliable then we should be able to relate the behavior of solid resins to their expanded counterparts. At least a relationship should exist between orientability (extensibility) and expandability.

For example;

1. The volume and stability of a free blown film sphere prepared on a modified free blown film apparatus (Figure 1) should be related to the rate of orientation, viscosity of resin, pressure of expansion and degree of cure.

These data should also be related to the expansion process, i.e., foam stability, rate of expansion, effect of melt viscosity on density and possibly the mechanical properties of the foam.

2. The relaxation of the stretched film may perhaps influence the heat distortion and the final mechanical properties of the foam.
3. The tensile properties of the stretched film should be related to the tensile properties of the expanded composite and the mole fraction of resin in the composite. One would also hope for agreement between materials prepared at the same strain rates.
4. Foam stability may be analogous to the stability of the film at rapid extension rates, or the maximum extensibility of the film (volume of the sphere) may be correlated with foam density and stability.
5. As the rate of orientation is increased one would expect the films to become stronger and as the rate of expansion is increased one would expect stronger foams, and perhaps, more oriented foams.

To summarize; these two processes (orientation of film and expansion) probably have common laws that govern their performance. For example, one would certainly expect the stresses generated in both systems to depend on the rate of strain and melt viscosity of the resin. For example;

$$S = \phi(u, \gamma)$$

Equation I

S = stress

u = melt viscosity

γ = strain rate

The following sections contain a more detailed treatment of the relationship between film orientation and foam expansion.

4. Effect Of Melt Viscosity And Cure

For a given resin system one would predict that as the molecular weight or melt viscosity increases more stress must be exerted to obtain a given strain, or higher pressure would be required to get equivalent expansion.

As the molecular weight of the resin (melt viscosity or degree of cure) increases the less volume one would observe in an oriented free blown film and the more dense the foam would be at constant temperature, pressure and blowing agent concentration.

In Figure 2 we have recorded the volume of the oriented polyethylene sphere produced on the free blown film apparatus using a .915 D polyethylene crosslinked with L-130 (2,5 dimethyl, 2,5 di(tert butyl peroxy) hexyne) at various degrees of cure. Film temperatures at the beginning of expansion were 100°C and 130°C.

The volume of an oriented bubble therefore, is inversely proportional to the degree of cure.

The phenomenon is also observed in the expansion of LDPE crosslinked with L-130 to different levels of cure and expanded with azodicarbonamide (K-150) blowing agent. Figure 3 shows that the cell size of the chemically crosslinked foams decreased with increasing

degree of cure. LDPE foam was compression molded and expanded at 2000%/<2 seconds. Samples of foam were removed and analyzed for density, gel and cell size.

In both Figure 2 and 3 there is a common trend toward narrower distribution of cell size and sphere size at the higher degrees of cure. This indicates that the more stable foaming system exists at ~25% gel then 10% gel for a .915 D polyethylene. One would hope that the point of greatest film sphere stability (largest volume) would appear in the same region as that observed for greatest foaming stability as we shall see later, there is a correlation.

Figure 4 again, illustrates the effect the degree of cure and melt viscosity have on the density of the foam.

Once more we have general agreement with a decrease in sphere or cell volume, and on increase in density as viscosity increased.

The data contained in Figure 2 is obtained by keeping the pressure constant in the free blown film apparatus and removing the heat source just prior to expansion. The blowing agent concentration remained constant in the expansion experiments recorded in Figure 3 and 4.

Films oriented on the modified free blown film apparatus can be evaluated by the following equation.

$$\text{Orientation} = \frac{\text{Surface area of the sphere}}{\text{Surface area of initial plaque}} \quad \text{Equation II}$$

The surface of the sphere was calculated by measuring the volume (volumetrically) of the sphere and calculating the surface area. The change in area was between 9 and 20 X. As we increase the volume of the spheres by increasing pressure. The spheres generally become less stable. Low density thermoplastic foams .03 → .06 gm/cc are less stable than the higher density foams. The expansion of a foam was calculated by Equation III.

$$\text{Foam Expansion} = \frac{\text{Volume of foam}}{\text{Volume of resin}} \quad \text{Equation III}$$

Foam expansion was maintained between 10 X and 25 X.

5. Effect Of Strain Rate

If Equation I applies to spheres prepared on a modified free blown film apparatus in addition to the expansion of polymers, then we could perhaps, expect foams and films prepared at different rates of extension or expansion (same resin or curing system) to have different tensile properties. For example, foams and films expanded at low rates of extension could be expected to be less stressed (due to relaxation, etc) and perhaps have lower strength than the more stressed samples produced by high rates of extension or expansion. This has been shown in films stressed at the same temperature but at different rates of strain.

In Table I we have shown how changes in the rate of strain effected the stress.

Corresponding crosslinked films of LDPE exhibit this same phenomenon. For example:

LDPE stretched 9X at 100°C in 10 seconds had a tensile strength of 1750 psi with 400% elongation. (No yield point)

LDPE (cured with the organic peroxide to 60% gel) stretched 9X at 100°C slowly, (approximately 10 seconds) had a tensile strength of 2500 to 3500 psi with approximately 250% elongation at failure.

LDPE (cured with an organic peroxide to 59% gel) stretched 9 - 10X at 100°C in <2 seconds, had a tensile strength between 7-10,000 psi with 7-10% elongation at failure.

Perhaps one could also predict that foams, prepared at different rates of expansion would possess different tensile properties. If our theories hold, films and foams would exhibit similar trends.

This phenomenon is more evident in high density polyethylene than in low density polyethylene, for example:

TABLE I

<u>Resins</u>	<u>.95D - 4 MI Eth-But Phillips Co-polymer</u>	<u>.96D - 4.7 MI Eth. Homo- polymer (Phillips)</u>	<u>.915D Ethylene Homopolymer 1.6 MI</u>
Stress At Failure (23°C)	(psi)	(psi)	(psi)
Strain Rate At (500%/min.)	3900	4500	2200
Strain Rate At (50%/min.)	3100	3900	1750

Figure 5 compares the tensile strength of low density PE foams (.915D - 1.6 MI) that were expanded by the chemical method (organic blowing agent) and physical method (Freon). Polyethylene compositions containing chemical blowing agents expanded in less than 2 seconds. Resins containing Freon blowing agents expanded at a slightly slower rate. We believe the close agreement in physical properties is due to the similar expansion rates.

The data in Figure 6 describe the tensile strength of high density polyethylene foams prepared at different rates of expansion. The tensile strength vs. density curve (volume fraction of polymer in foamed composite) shows that the higher strained samples are stronger. Immediately the question of orientation arises. The same foaming system was used to remove as many variables as possible. However, other similar trends were also observed, that is, the higher strain rates involved higher pressures.

We have consistently noted that foams produced at higher strain rates were stronger. The data are more conclusive in high density polyethylene and polystyrene.

Figure 7 compares polystyrene foam prepared by the slow molding process and by extrusion. The expansion cycle in the molding process was >4 minutes while the expansion cycle in the extrusion process was completed in <5 seconds. The data in Figure 7 imply that the extrusion foamed material is more stressed and perhaps more oriented. Certainly, the more stressed samples were stronger.

Again we see the phenomenon that an increase in expansion rate improves foam properties. Foams prepared at higher rates, from resin of higher molecular weight or higher crosslinked density should be stronger. The data in this section prove that they are stronger.

6. Foam Stability

If our concept of foam structure can be described as an infinite series of biaxially oriented cells, then to be consistent, the behavior of films during orientation should give an indication of foam stability. In our previous discussions⁽⁶⁾ we have shown that the stability of low density foams is a function of degree of

crosslinking. Figure 8 illustrates the stability of low density PE foams prepared at high rates of expansion using azobisformamide as the blowing agent. (Figure 9 and 10) show the same data plotted on log normal paper which follows a Gaussian distribution for % solubles or % gel. (This takes into account the errors in extraction, etc). At high rates of expansion different stability relationships exists for low density PE (10-20%) and high density PE (30-40%). Experiments with the biaxial orientation of crosslinked tubes and plaques at high rates of extension shows similar effects.

For example; the stability of an oriented sphere prepared at high rates of expansion on a free blown film apparatus, increases as one crosslinks to higher levels of cure. This can be seen in Figure 11. The width of the stability envelope for LDPE is an indication of stability at high rates of extension. It is in general agreement with the stability during expansion of the same resin in the production of foams, (Figure 10). The increase in the degree of cure increases the elasticity of the resin and allows one to freeze and as a result to produce in more stresses, a stronger, more oriented film. Additional pressure must be exerted to expand the more cured systems to obtain equivalent volume.

This same phenomenon exists for linear PE. The more crystalline polyethylene resins have, a higher modulus and in general, are more difficult to expand. This has been shown previously in Figures 8 and 9 where an increase in gel over low density polyethylene foams was required for stability. Crosslinked linear polyethylene films oriented at high rates of extension on the modified free blown film apparatus show a peak sphere stability in the same region as optimum foam stability. For example, Figure 12 shows the effect of crosslinking on sphere stability (% not ruptured) for a number of consecutive runs. The threshold region for sphere stability appears between 30 and 40% gel. As we saw in Figures 8 and 9 the "threshold stability" for expanded high density polyethylene is at 30 and 40% gel.

The effect of gel on the elasticity of the system can also be seen in Figure 13. Figure 13 shows the effect of gel on the elongation at failure of cured films. Again we see a definite correlation between the mechanical properties of films at room temperature (Figure 13) during orientation between 100-150°C and foam stability (170-200°C).

One must conclude from the data presented here that a study of film orientation can give one an insight into resin "foamability". In fact, a close analysis of a film system should allow one to predict resin behavior during expansion.

7. Theoretical vs. Observed Values

The effect of density (volume fraction of the resin in the expanded composite) on the mechanical properties of olefin foams has been investigated. The increase in strength and flexural modulus of elastomers with increasing concentration of the polymer in the composite (density) has been theoretically discussed by Gent and Thomas⁽⁸⁾ using the fundamental principles of mechanics. The properties have been quantitatively related to the properties of the polymeric phase and its concentration.

We have discussed the expansion of polyethylene using various processes.^(3,5,6) The mechanical properties of the foams have been related to their volume fraction concentration in the foam (density). We have also pointed out that a variety of multi-phase polymer blends could be co-crosslinked and expanded.⁽⁵⁾ The properties of these grafted systems also depend on density or the volume fraction of the resin present.

To our knowledge there is no comparable data available in the literature that describe the variation of properties for polymer blends or modified low density polyethylene foams prepared from linear or branched polyethylene; or analyses their structure.

As we indicated previously, this paper describes our attempts to analyse the expansion of thermoplastics and the resulting product on the basis of film orientation.

We have compared the properties of polyethylene and polystyrene foams prepared at different rates of expansion, (see Figure 5 and 6). In Figures 14, 15 and 16 we have compared these mechanical properties with those one could theoretically predict on the basis of the unexpanded resins converted into films at equivalent rates of orientation (strain), unoriented "relaxed" films and the molefraction of the resin in the matrix.

Figure 14 shows that the tensile strength of the low density polyethylene foam is directly proportional to the volume fraction of the resin present in the expanded composite. From the data in Figure 14 one can immediately see that the crosslinked low density PE foam properties agree with those theoretically predicted for a foam based on relaxed uncrosslinked film. If the cells are made up of a series of tiny biaxially oriented films then one would expect better properties which would agree with the values in curve A, rather than curve C. Analyses of the foams shows little difference between the physical properties (tensile strength) of extruded Freon expanded LDPE foam, extruded Celogen OT (4,4' oxybis benzene-sulfonyl hydrazide) expanded PE or azobisformamide expanded and crosslinked LDPE foam.

The strange fact is that all the properties vary linearly (log-log plot) with the uncrosslinked polyethylene cast film. The agreement is quite good.

The effect of rate of expansion is more pronounced with the high density polyethylene foams described in Figure 15. Although the foams prepared at higher rates of expansion were stronger, their properties approached the theoretical values predicted for chemically crosslinked cast film (unoriented).

Figure 16 also shows the same general trend for polystyrene foams. Foams prepared at higher rates of expansion were stronger but were less than those predicted for "oriented" foams.

One of the reasons for this anomolous behavior (the mechanical properties of a foam do not show any orientation effect) may be that the tensile strength is a measurement of the weakest part of the foam. This weak point may be several torn windows that initiate a tear and produce lower tensile values. It is common knowledge that as films become more oriented the tensile strength increases but the elongation at failure and tear strength decrease.

It is extremely difficult to evaluate orientation in foams by these methods. The paradox is that the mechanical properties of the foam are related to the base polymer that has not been prepared at the same rates or (as in the case of LDPE), cured. For example, a polyolefin film having the same structure as those observed in the foams and biaxially oriented at the same rate of expansion produces a high strength film. The tensile strength (measured on the foam) is much lower than one would predict (based on density).

The enhanced mechanical properties of the oriented films over unoriented films may be the result of stresses frozen in shape at the crystallization temperature. The films prepared on our free blowing apparatus cool off rapidly upon expansion. We have seen good agreement between the orientation behavior of films and the expansion behavior of the base polymers. Although the low density foams are expanded at the same rate of strain as the films are oriented, the lack of agreement in properties between solid and expanded resin may be caused by the stress relaxation of the expanded composite during cooling.

8. Effect Of Relaxation On Film And Foam Properties

The LDPE and HDPE foam (Figures 14 and 15) properties lie on a straight line and extrapolate to the mechanical properties of a cast unstressed film or a film that has relaxed.

The main question one must answer is "why aren't these foams stronger"? They are expanded at rates that approximate impact velocities. Perhaps the key lies in Figure 17.

As a film is stressed at higher and higher temperatures on a free blown film apparatus the amount of unrestrained relaxation (shrinkage) decreases when the oriented film is reheated to its m.p.

The films in the cell windows may be highly oriented initially, but then become relaxed when the foam slowly cools off. Most of our foams were prepared between 160 - 190°C.

Figure 18 describes the effect of annealing a high strength oriented film at elevated temperatures at constant strain. Attempts were made to reproduce the cooling cycle of the foam as much as possible. The tensile strength deteriorated almost to that of the original chemically crosslinked film. This apparently is the reason for the lack of strength in the expanded composites. To check ourselves, another method of measuring orientation was investigated.

9. Birefringence Of Foams

Film orientation can be measured by determining area shrinkage and shrink tension vs. temperature. So far we have not been able to determine the shrink behavior of the cell walls in the foams or to use this method to determine orientation. Another method is the use of birefringence measurements.

Linear and branched PE foams were examined using a Polarizing Microscope with a Leitz Fiber Measuring Eyepiece. Samples were sliced into portions containing cell walls and/or struts. It was necessary to make the samples thin, otherwise, they would not transmit light. Table II lists the results obtained for an average of three measurements.

Sample 1 is relaxed, therefore, no birefringence.

Sample 2 is a highly oriented crosslinked film. The % shrink is >90% at the m.p. and shrink tension is >150 psi. Therefore, there is little doubt that Sample 2 is highly oriented. The lack of birefringence is due to the balanced orientation.

TABLE II

BIREFRINGENCE DATA

<u>Sample Description</u>	<u>Rate of Extension</u>	<u>Temperature</u>	<u>Birefringence⁽¹⁾</u>
1. Hot Blown LDPE Film	3x/3 sec.	150°C	Zero
2. CCL LDPE Film	4x/<2 sec.	120°C	Zero
3. LDPE Foam (Ext.)	5x/<2 sec.	160°C	6 x 10 ⁻⁵
4. CCL LDPE Foam (C.M.)	5x/<2 sec.	185°C	8 x 10 ⁻⁵
5. CCL HDPE Foam (C.M.)	4.5x/<2 sec.	185°C	4 x 10 ⁻⁵
6. CCL HDPE Foam (Ext.)	4x/<30 sec.	-	10 x 10 ⁻⁵
7. CCL HDPE Foam (Atm.)	4.5x/<60 sec.	200°C	6 x 10 ⁻⁵
8. HDPE Fiber Melt Orient	Extruded Fiber	175°C	8 x 10 ⁻⁵

(1) Maximum difference in refractive index.

Foams 3 to 7 are prepared by various processes; for example, endothermic blowing agent (No. 3) exothermic blowing agent (4, 5, 6, 7) - extrusion foamed (3, 6) compression molded and expanded - (4, 5) and slow expansion (7). In no case do we see evidence of orientation.

This does not mean there is none since the possibility of biaxial orientation yielding zero birefringence still exists. However, I believe it safe to say that our tensile data, relaxation data and birefringence data strongly indicate that the final foamed structures are not oriented.

10. Effect Of Blowing Agent

One would hope that if the foams consist of highly oriented cells immediately after expansion and subsequently suffer a loss in strength due to relaxation that a heat sink would be appropriate as a blowing agent. Foams prepared with refrigerants as blowing agents had similar physical properties as those prepared from an exothermic blowing agent "azobisformamide".

Ralph Hansen and W. M. Martin⁽⁹⁾ have described their "hot spot" mechanism.* "The decomposition of azodicarbonamide is highly exothermal. Since it is not very soluble in polyolefins and since it decomposes at a rate which is compatible with the extrusion process, azodicarbonamide has been described as a suitable blowing agent for the extrusion of expanded polyolefins. It is suitable because it creates many localized hot spots during its continued decomposition while the solution of gas in polymer formed by its partial decomposition emerges from the extruder. The many localized hot spots initiate many bubbles, and fine cell structure and high efficiency are observed".

ABFA may be ideal for producing small cells in foams, however, it may be a poor choice if one desires highly oriented structures. One feels the need for a heat sink to freeze in the stresses created by high

* Novel methods for the production of foamed polymers by Ralph H. Hansen and W. M. Martin, I&EC Prod. Res. Dev., Vol. 3-No. 2, 6/64.

strain rates. Perhaps the blowing agents are not used in sufficient quantity to get the effect.

11. Requirements For High Strength Foams

In the previous sections we have analyzed the expansion process and product as an extension of film orientation technology. Perhaps a more meaningful comparison of oriented film properties and foam properties can be obtained using the data in Figure 19.

The strength of the film increases with increased orientation and this could be expected to occur most at the lowest densities.

Theoretically, one requires no reinforcing by crosslinking to obtain uniform, maximum expansion of polymers. In fact, we have seen that it is most desirable to have an uncured foam to get maximum volume and lowest uniform density.

If high melt extensibility (high tensile and elongation) is essential, then regulating the temperature of expansion between narrow limits (as we do in the film orientation) should allow one to trap the maximum amount of gas and expand fully by closely adjusting the elastic properties of the system.

As we summarize our findings we conclude that a high strength "oriented" foam should have the following components.

1. Density - variable (depends on application).
2. Cell Morphology - less than .010", uniform oriented windows and struts.
3. Resin
 - a. low melt index
 - b. high activation energy of flow to create a large increase in viscosity upon expansion and cooling to stabilize foam and aid processing. (Figure 20 and 21 illustrate this).
 - c. orientation time must be short.
 - d. relaxation time must be very long, compared to c.
 - e. polymer must "set up" before it relaxes ($C \ll D$).
4. Additives - endothermic nucleators.
5. Blowing Agents - endothermic with high gas yield.
6. Process - very fast rates.

SUMMARY AND CONCLUSIONS

A technique has been developed that can be used to predict the expansion behavior of polymers. The "free blown film" technique is an effective tool that can be used to study the orientation of films and the expansion of polymers.

We have been able to relate foam stability, cell size and uniformity to film orientation.

Although low density foams were expanded at the same rate of strain as films were oriented there is a lack of agreement between the mechanical properties of the solid resin and the expanded resin (corrected for density). A possible cause for the poor agreement has been pointed out to be "stress relaxation" of the expanded composite. This is partially substantiated by; (1) The low tensile strength of foams, (2) Relaxation of oriented films at the process temperature and (3) Lack of birefringence.

A list of requirements is proposed for high strength foams.

ACKNOWLEDGMENTS

The author wishes to express his thanks to the W. R. Grace Research Division for their permission to publish this research. Thanks are also due to Mr. R. L. Adams who prepared the foams and helped develop the processes. Mr. C. Vollmerhausen and Mr. George Angelov who prepared the films. Mr. G. Fulmer who supervised the tensile testing of films and foams, and to Mr. I. C. Stone for birefringence data. Special thanks is due to Dr. James Cote for his help and our many discussions about orientation.

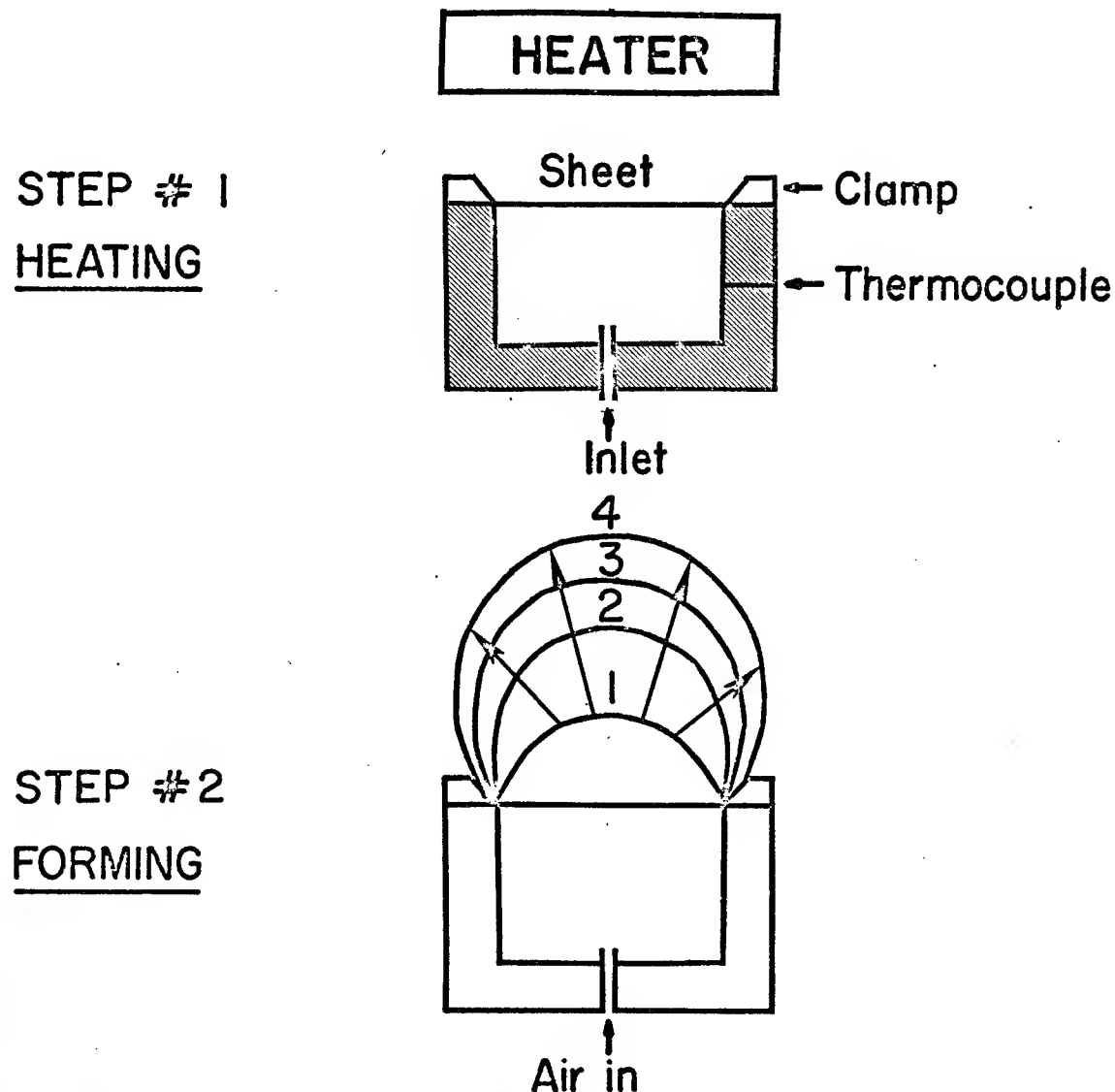
BIBLIOGRAPHY

1. Butzho, R. L., "Plastic Sheet Forming", Reinhold Plastic Application Series.
2. Adkins, J. E., and Rivlin, R. S., "Large Elastic Deformation Of Isotropic Materials", J. of Physical Soc., 5/1952.
3. Benning, C. J., and Nutter, J. I., "Filled Polyethylene Foams", Preprints 22nd. Annual Technical Conference, SPE, Montreal, Canada, March 7-11, 1966.

BIBLIOGRAPHY (cont'd)

4. Lasman, H. R., "Foaming Agents For Polyolefins", SPE Journal, 18, 1184-91 (1962).
5. Benning, C. J., "Polyethylene Foam I - Modified PE Foam Systems. "In Print".
6. Benning, C. J., "Polyethylene Foam II - Mechanical Properties of Polyethylene Foams Prepared at High and Low Rates of Expansion. "In Print".
7. Rubens, L. C., et al U.S. Patent 3,067,147 "Process for foaming and extruding polyethylene using Freon as a foaming agent".
8. Gent, A. N., and Thomas, A. G., 7th. Annual Technical Conference Proceedings, Cellular Plastics Division, SPI, New York City, New York, April, 1966.
9. Hansen, R. H., "Production of fine cells in the Extrusion of Foams", SPE Journal, 1877-82 (1962).

FIG. 1
FREE BLOWING OF FILMS ⁽¹⁾ & (2)



1. "Plastic Sheet Forming" R. L. Butzko
Reinhold Plastics Ap. Series
2. Large Elastic Deformations of Isotropic Materials
V. E. Adkins & R. S. Rivlin Journ. Phys. Soc. 7 May, '59

FIG. 2
VOLUME OF SPHERES VS. DEGREE OF CURE

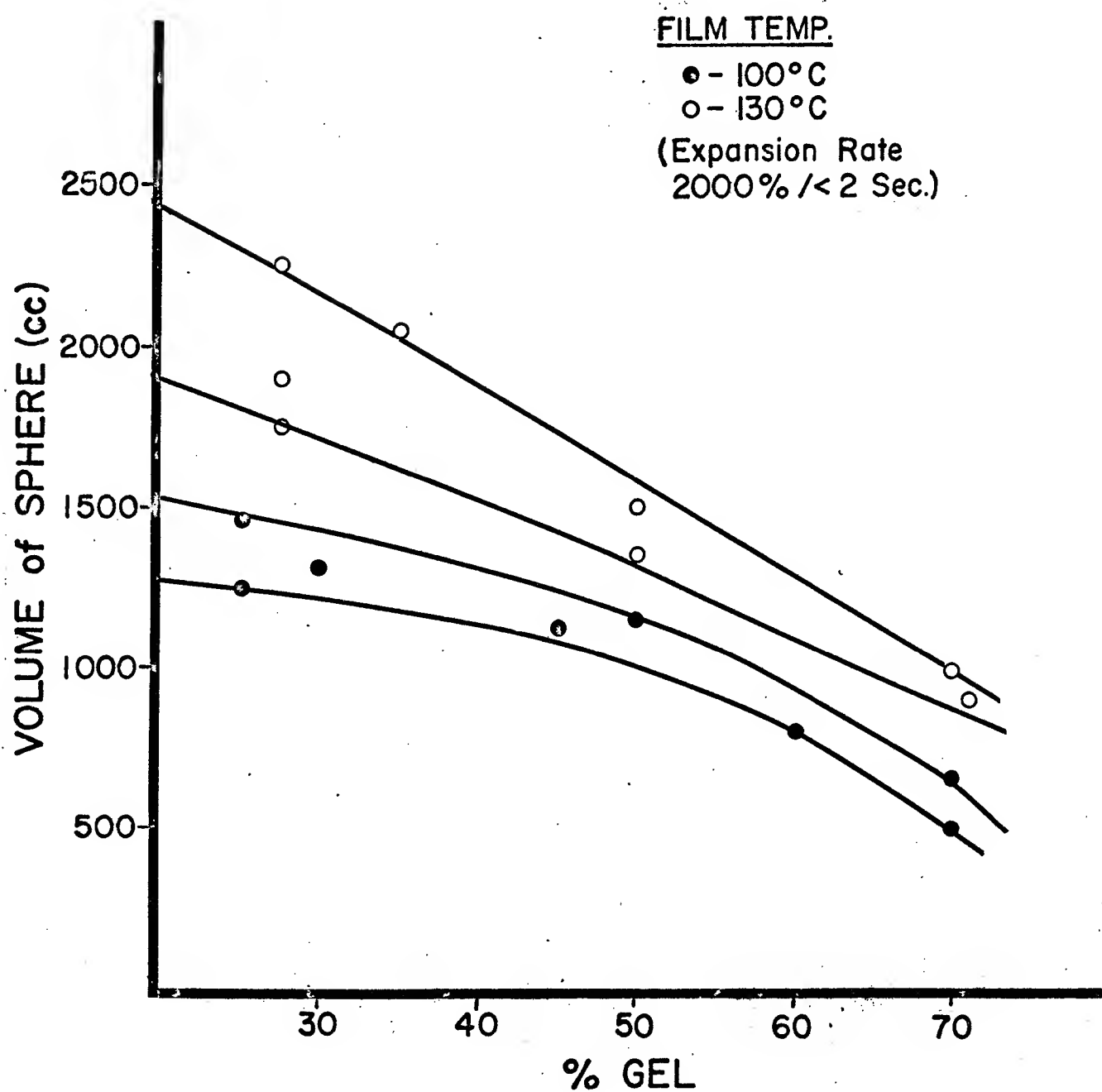
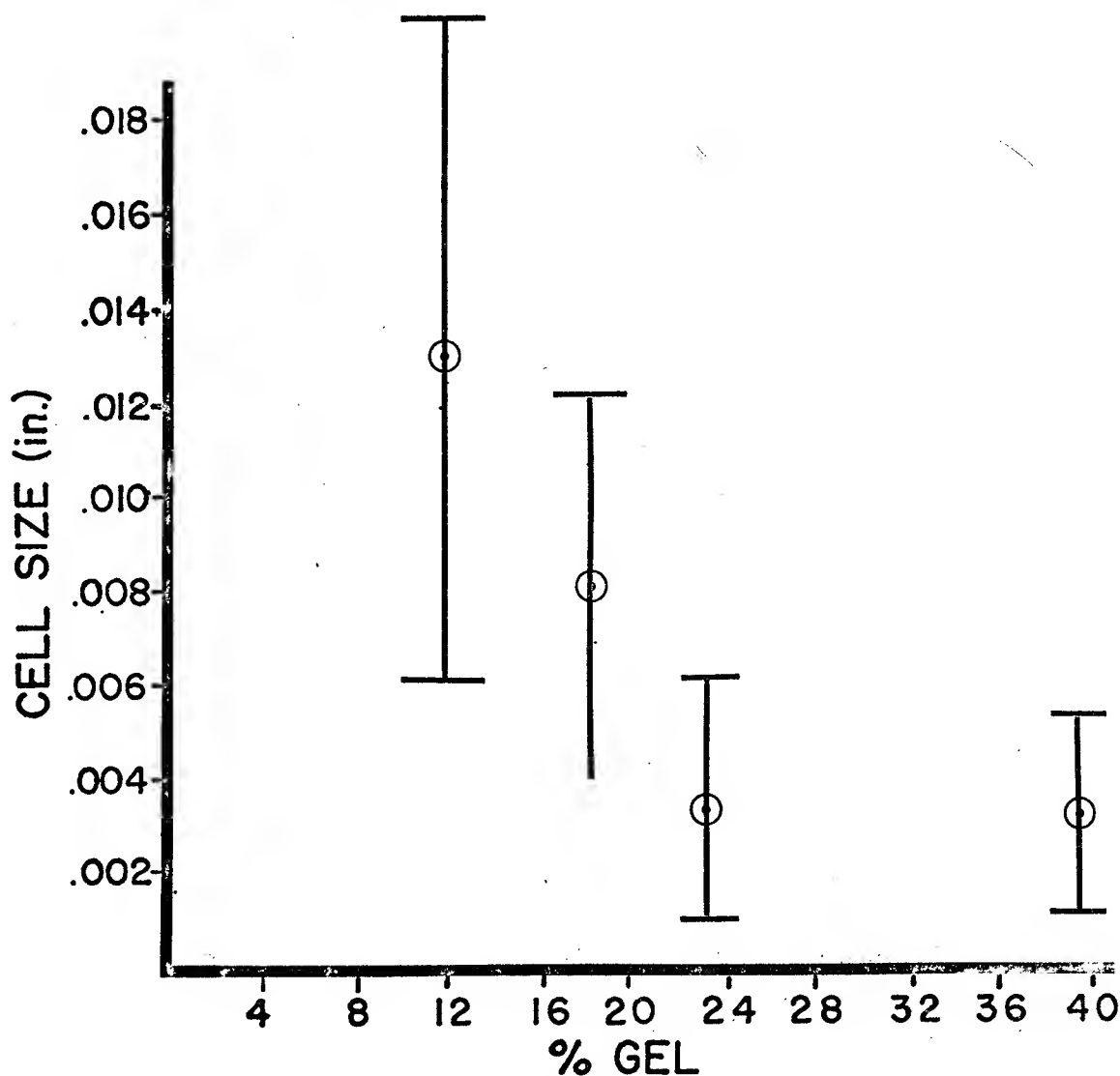


FIG. 3
CELL SIZE VS. DEGREE OF CURE



FORMULATION	DENSITY	CELL SIZE	% GEL
LDPE	.068	1-5 mil	38.8
(915 D 1.6 M. I.)		1-6 mil	22.4
ABFA 4 WT. %	.065	4-12 mil	18.6
L-130 .5 WT. %	.062	6-20 mil	11.8

FIG. 4
DENSITY VS. DEGREE OF CURE

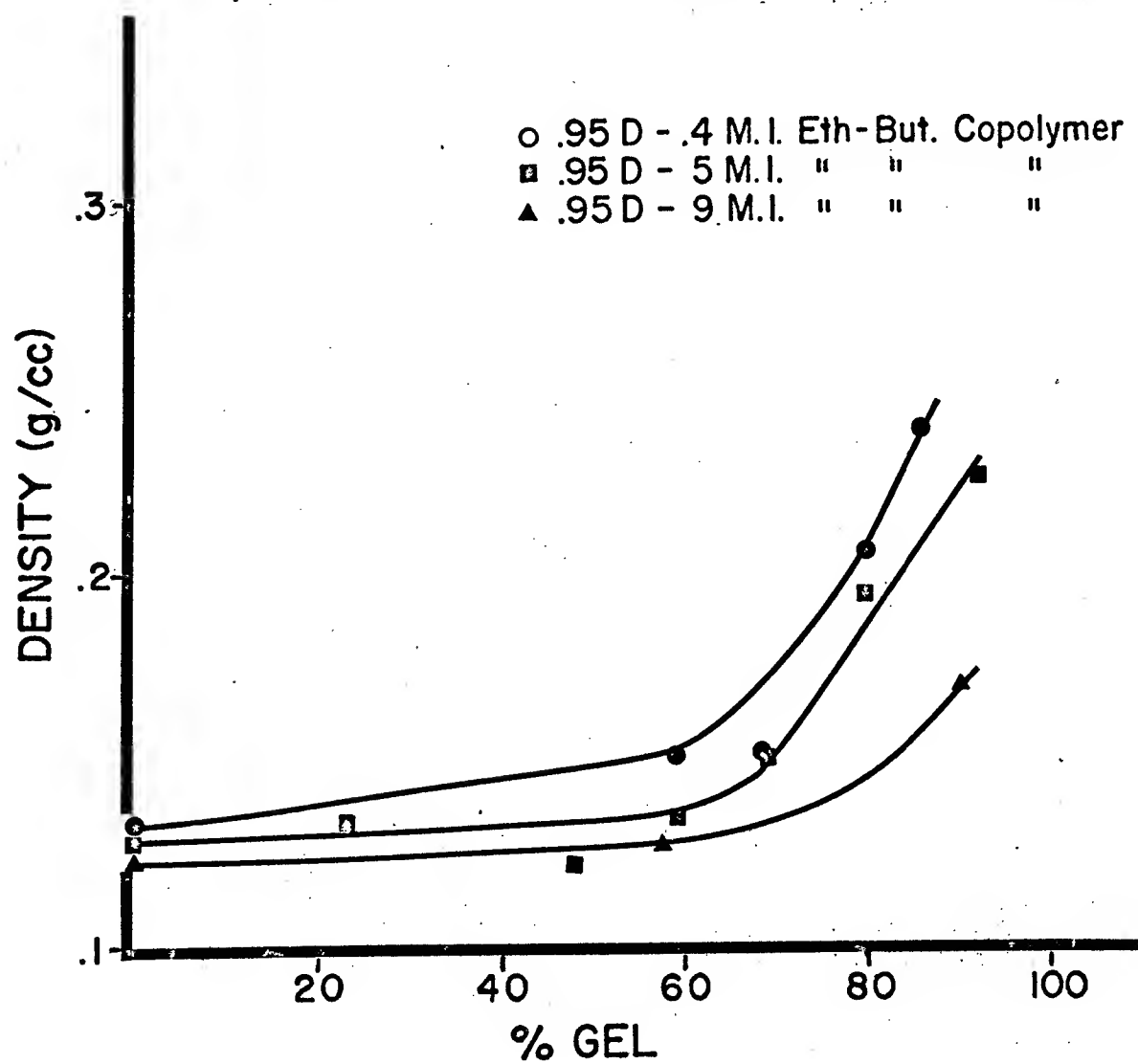


FIG. 5
DENSITY VS. PROPERTIES OF LDPE FOAMS

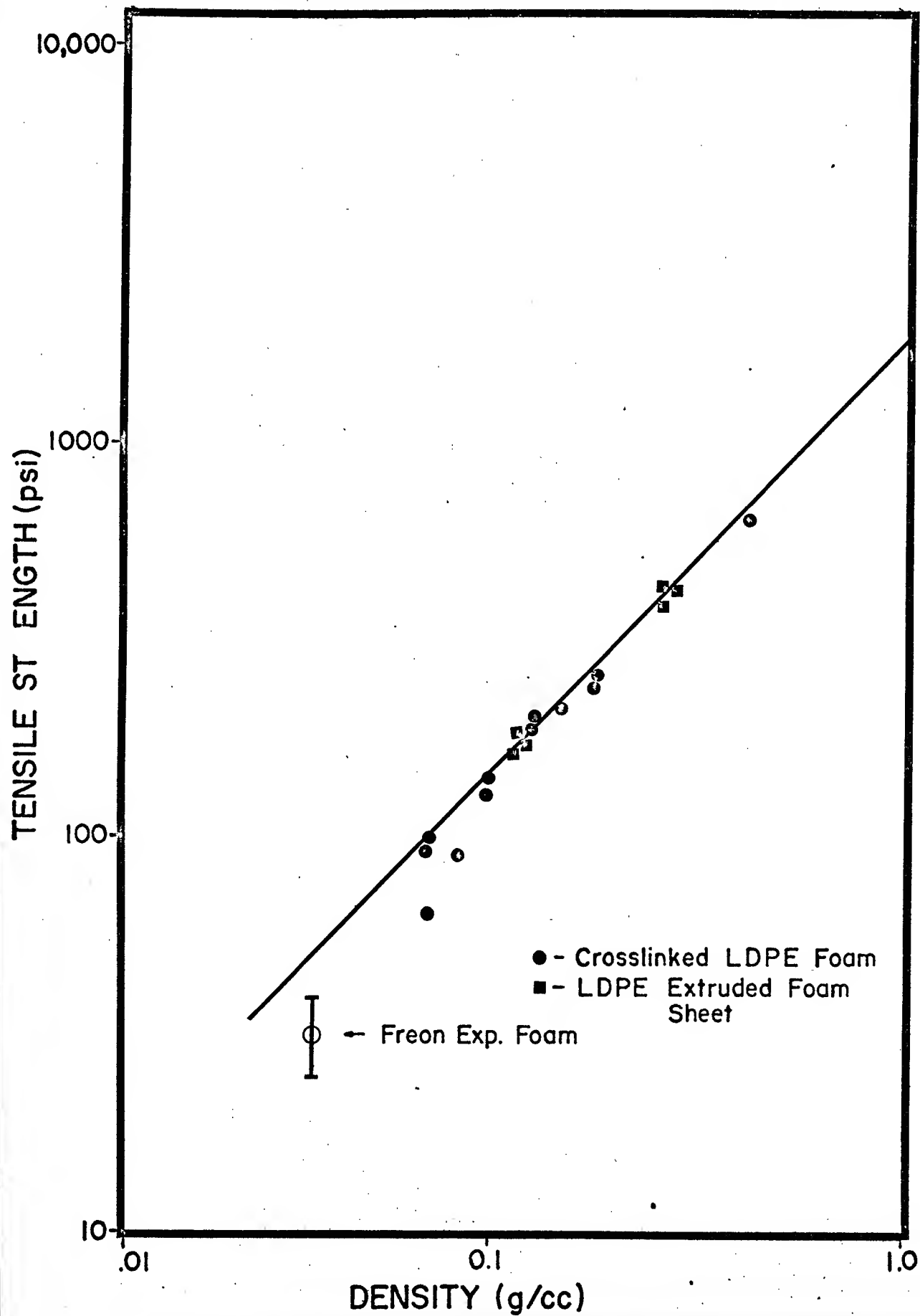


FIG. 6

DENSITY VS. TENSILE STRENGTH OF HDPE FOAMS

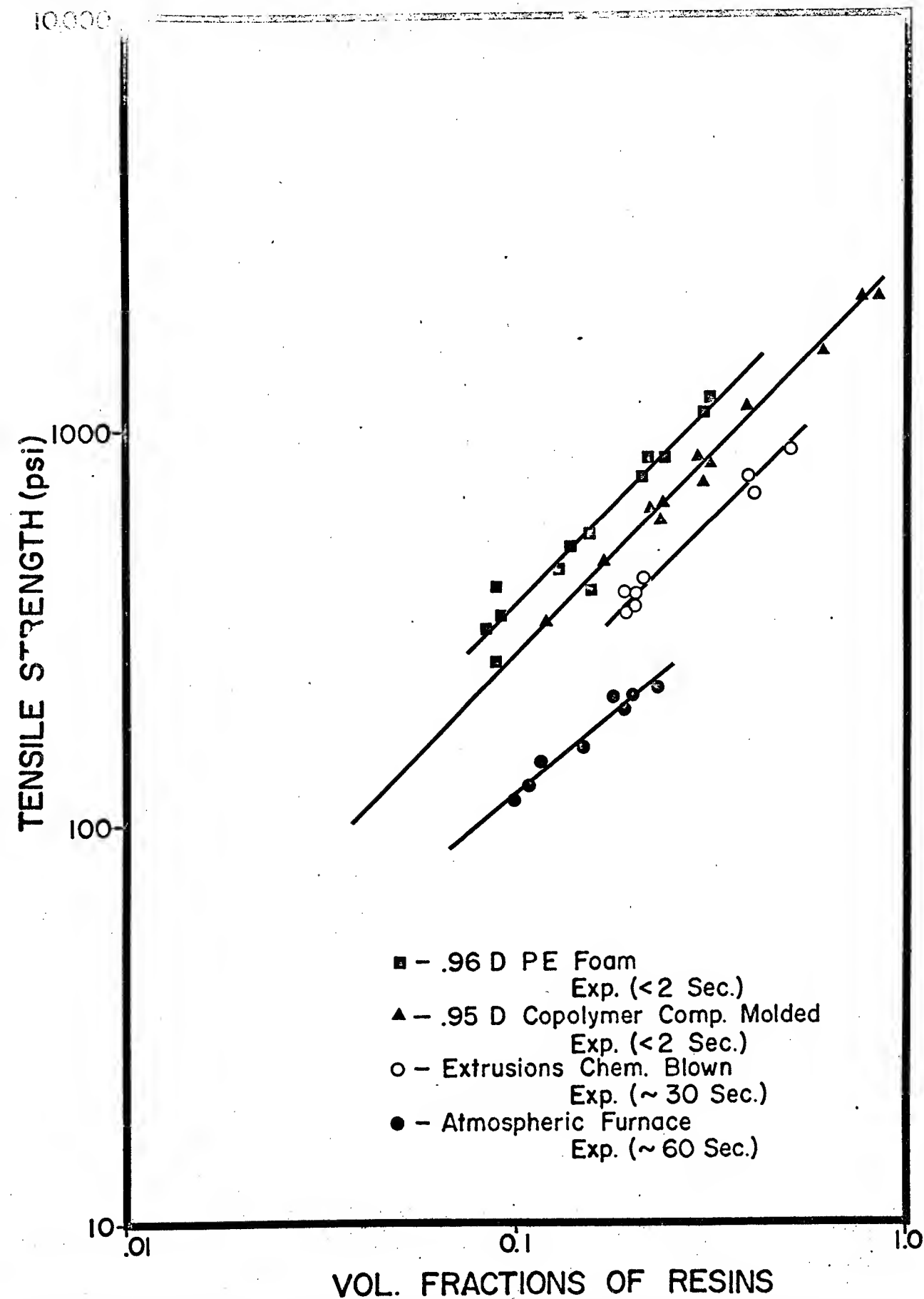


FIG. 7

TENSILE STRENGTH OF POLYSTYRENE FOAM

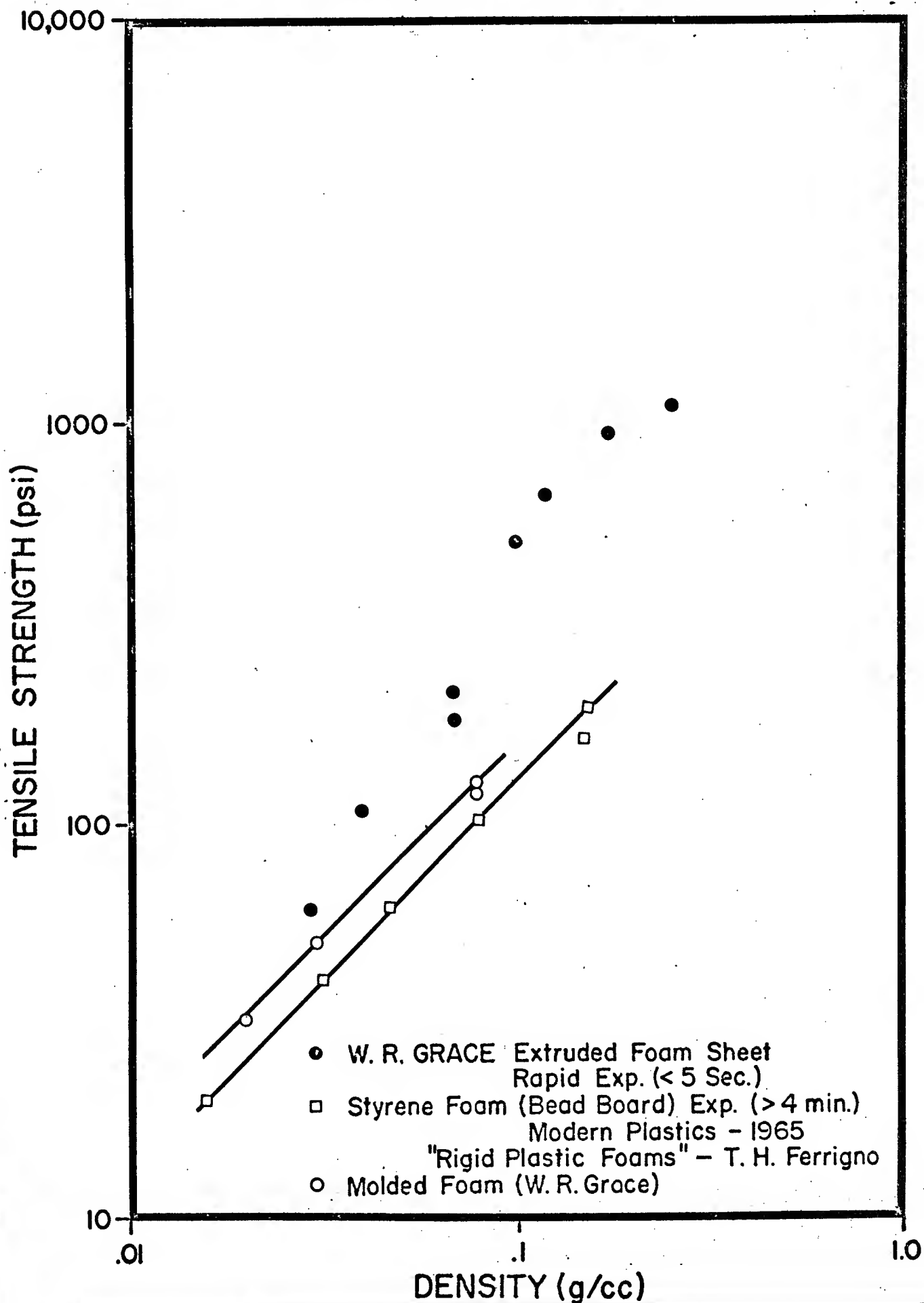


FIG. 8 STABILITY OF LOW DENSITY PE FOAM

EXP. RATE < 2 Sec.
DENSITY 0.06 - 0.1 g/cc

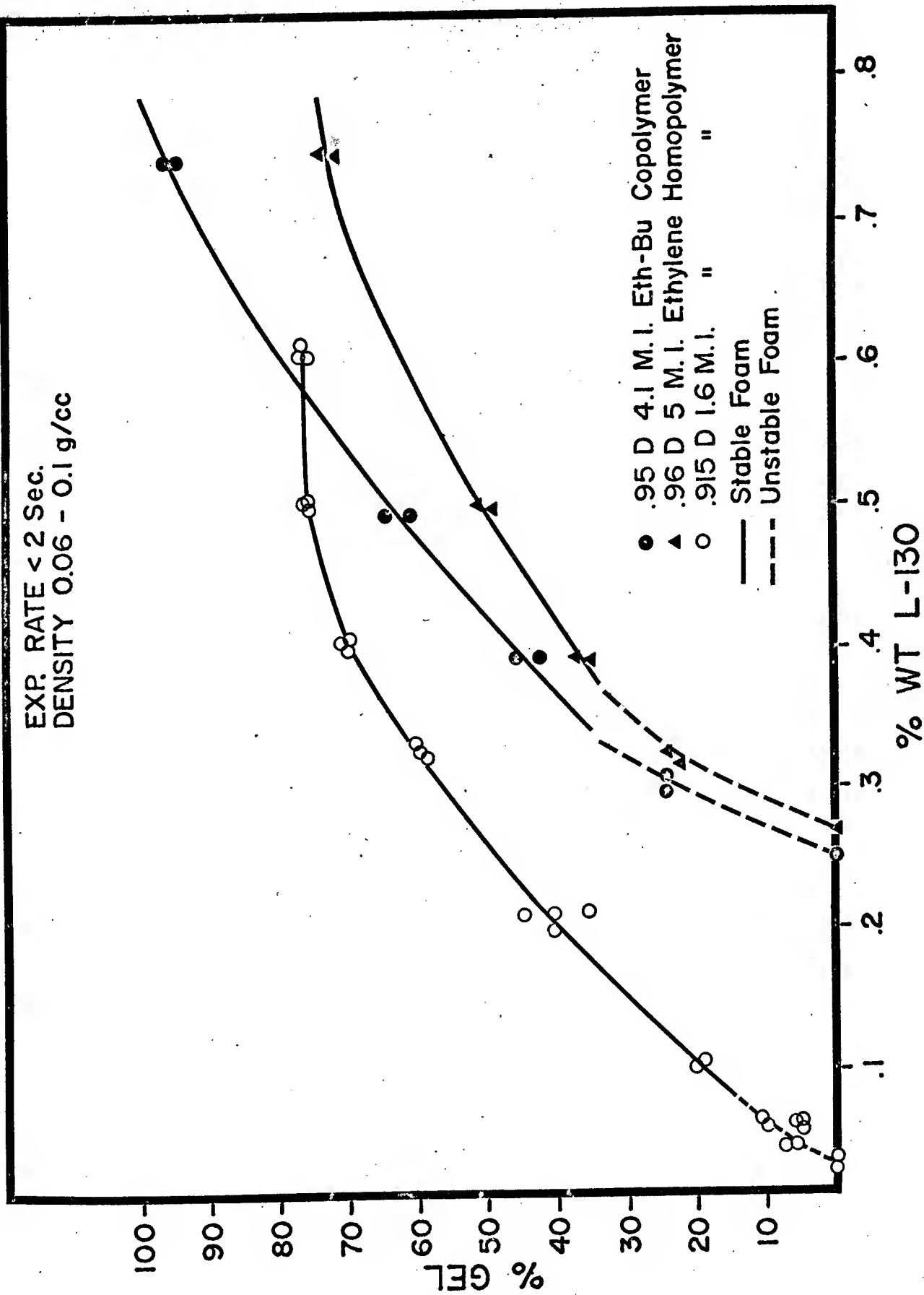


FIG. 9
STABILITY OF LINEAR PE FOAMS

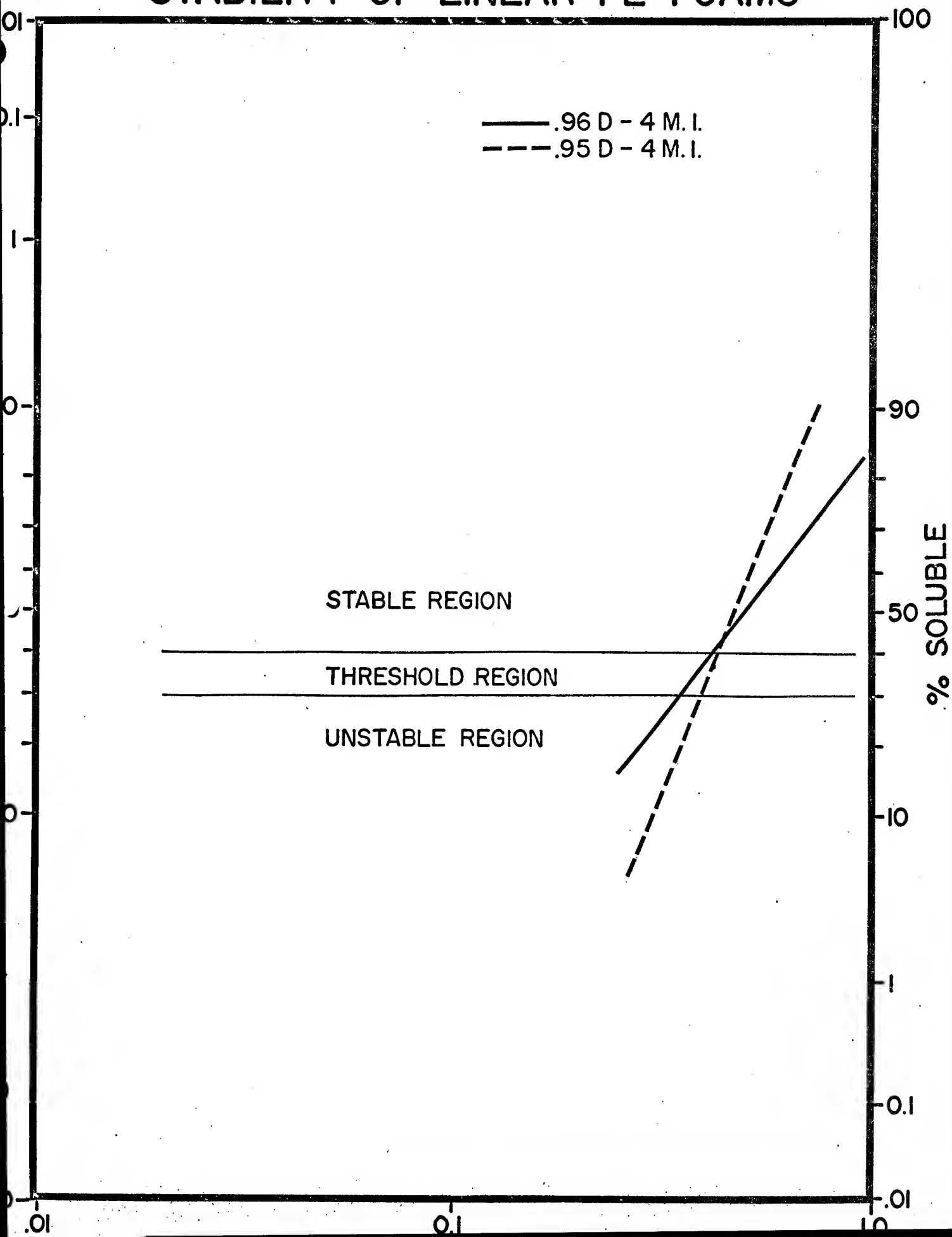


FIG. 10
STABILITY OF LDPE FOAMS

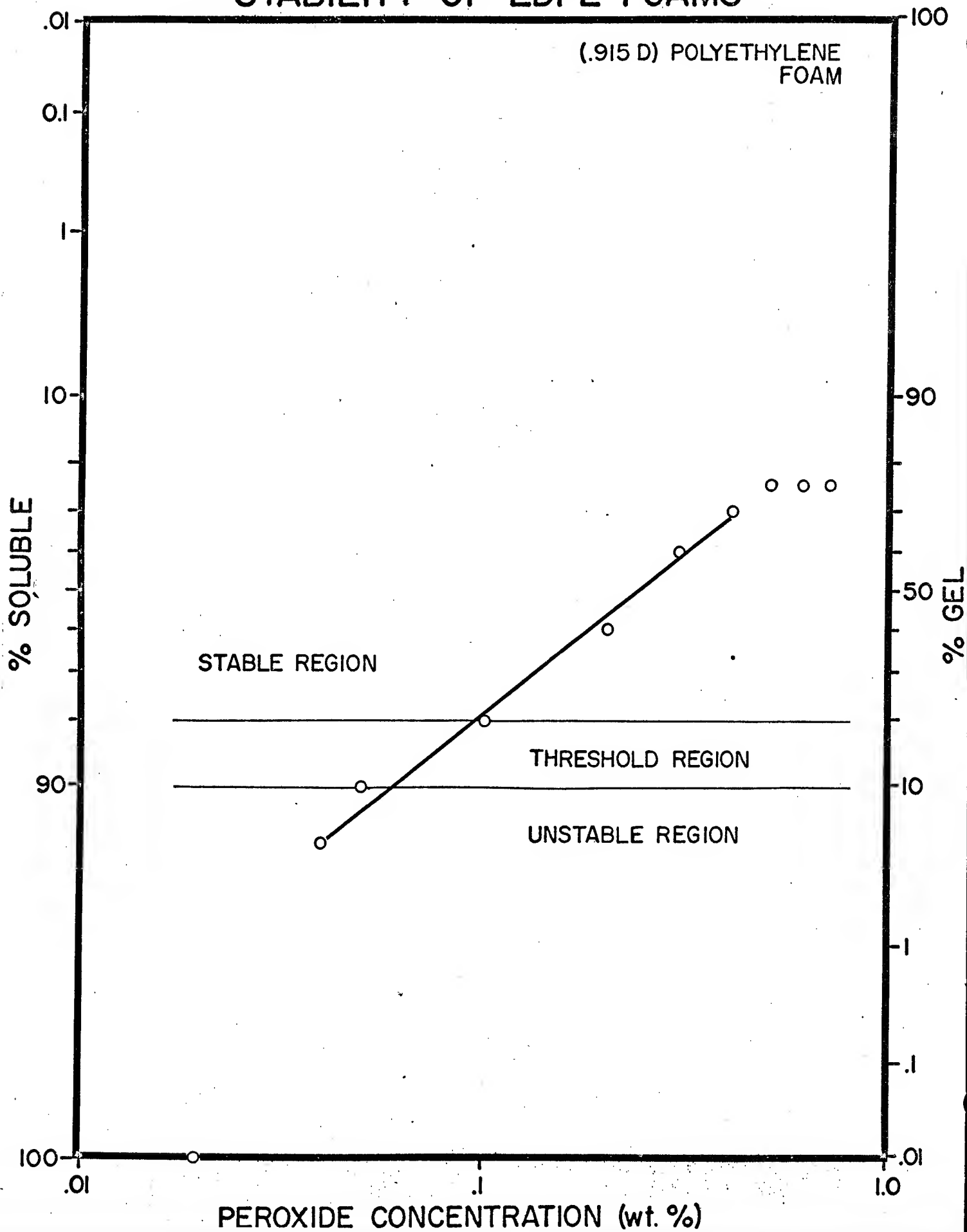


FIG. II
RELATIVE VOLUME OF FREE BLOWN FILMS

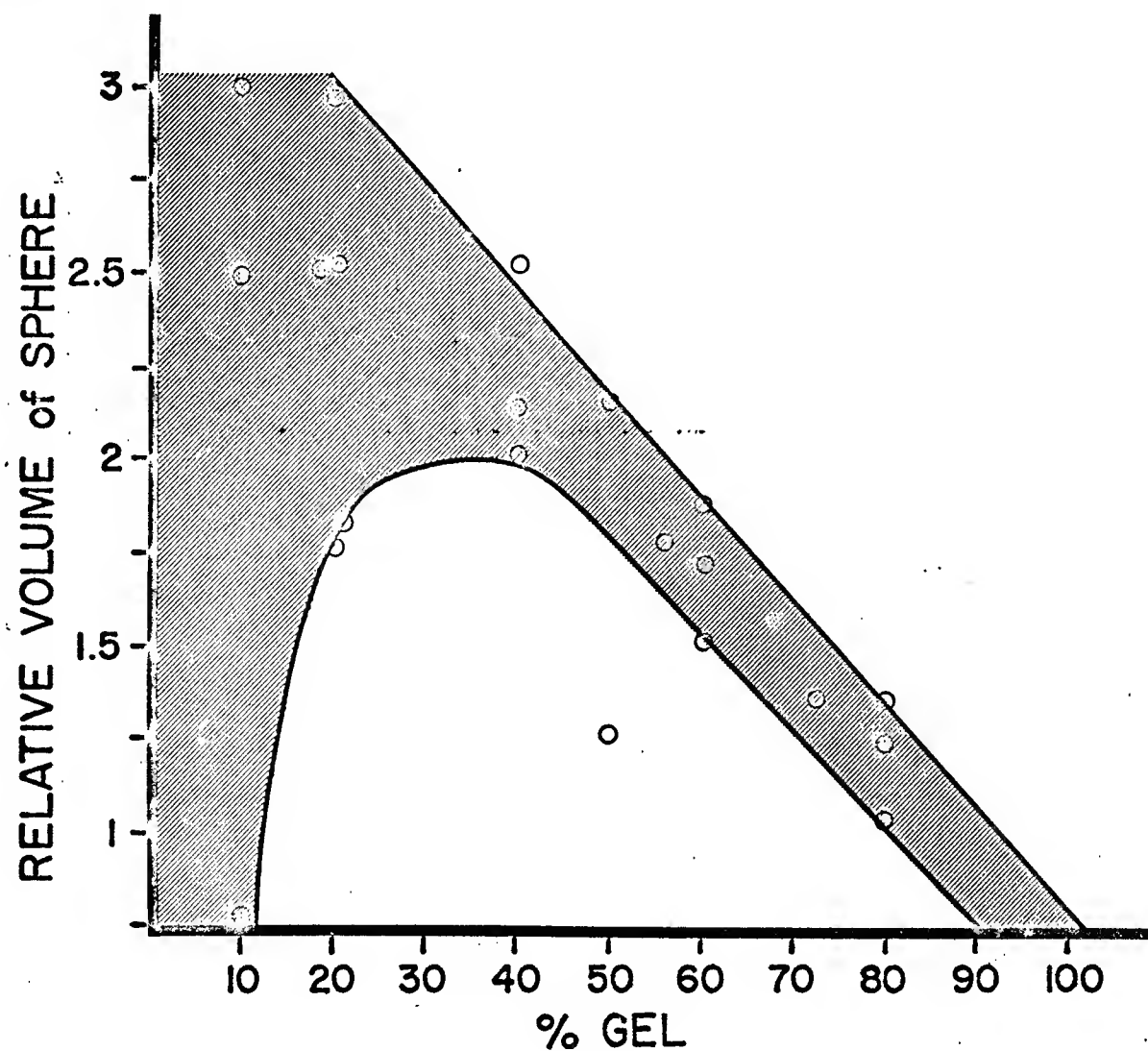


FIG. 12
SPHERE STABILITY OF CROSSLINKED HDPE FILM

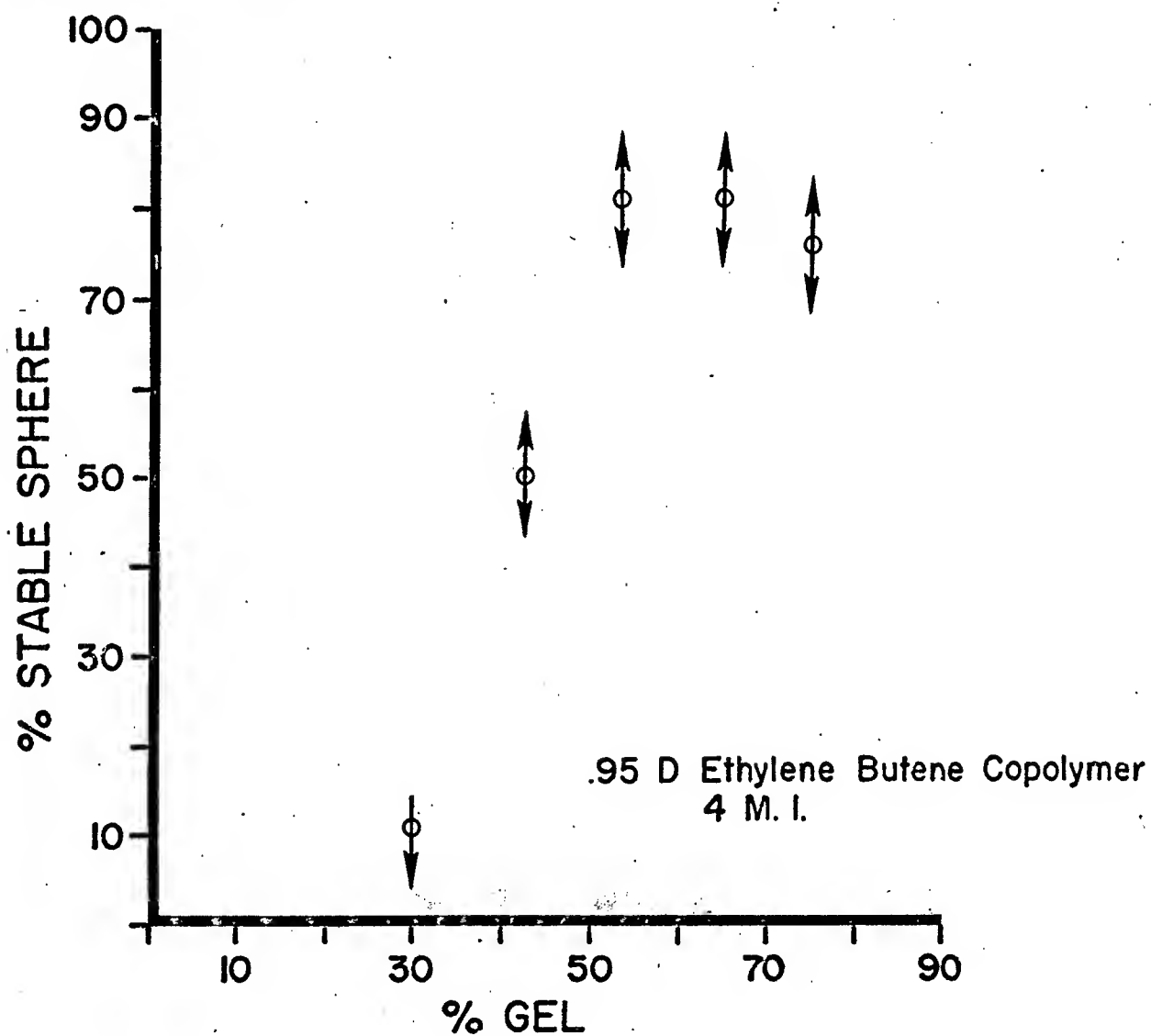


FIG. 13
CURE VS. ELONGATION AT FAILURE

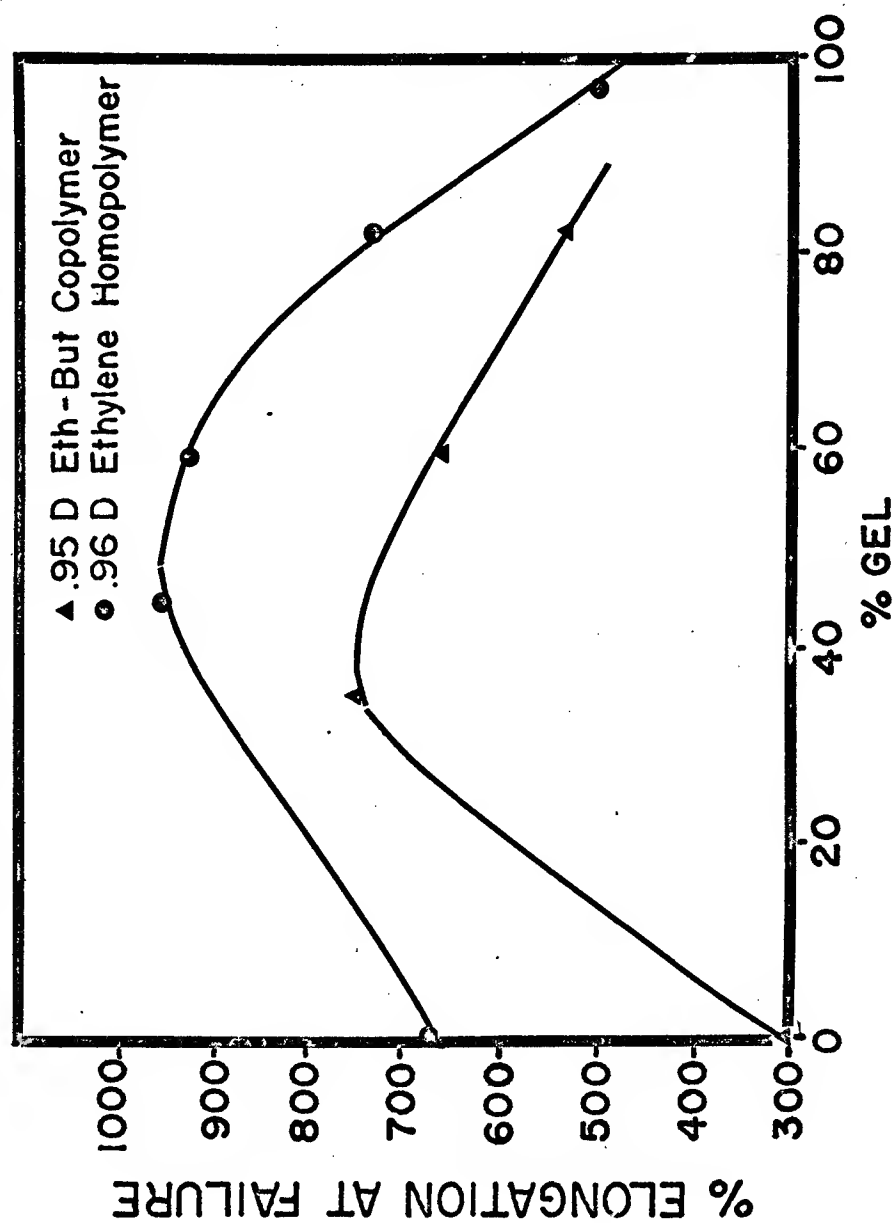


FIG. 14

PROPERTIES OF LDPE FOAMS (Theory & Obs.)

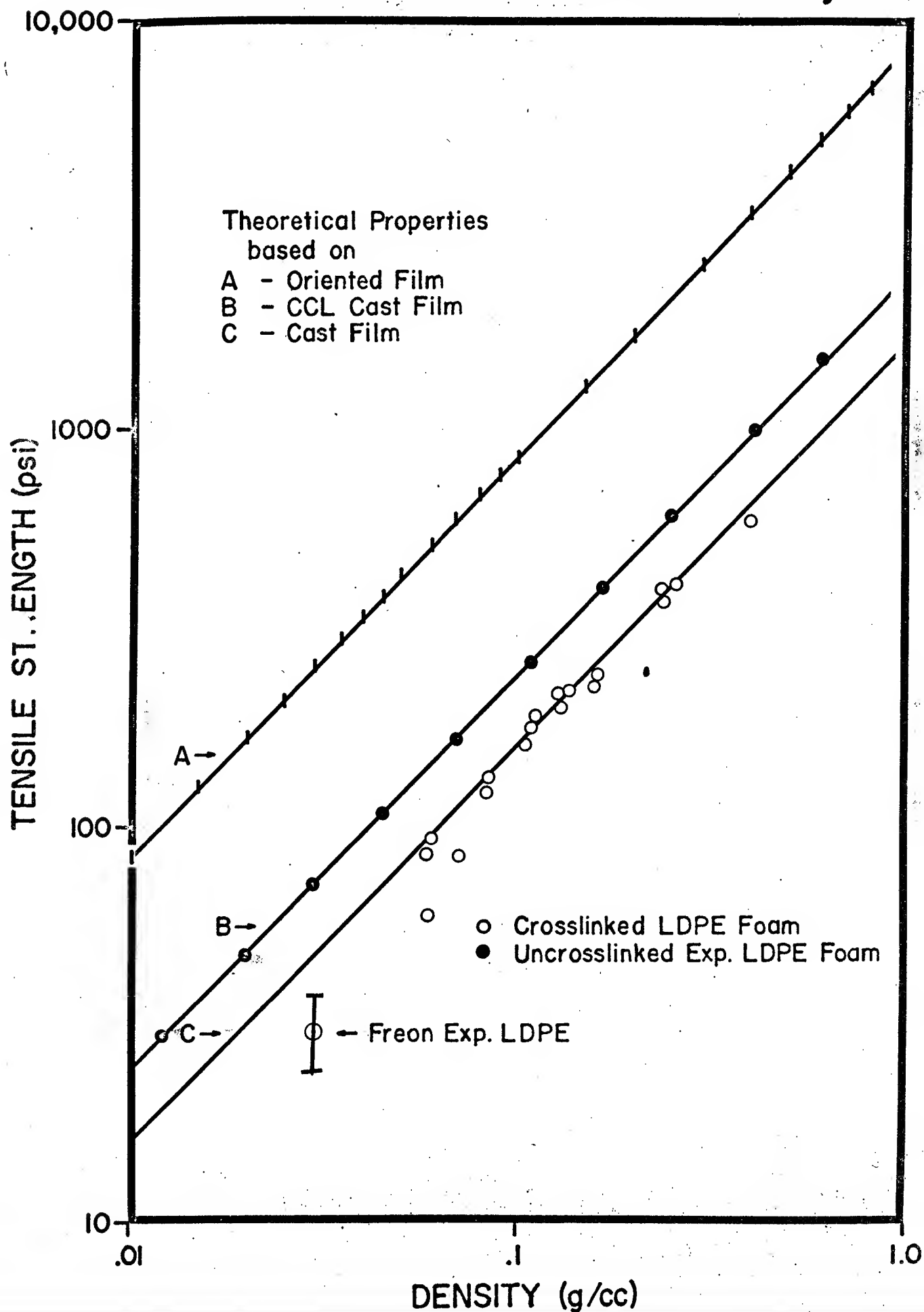


FIG. 15
 PROPERTIES OF LINEAR PE FOAMS
 (Theory & Obs.)

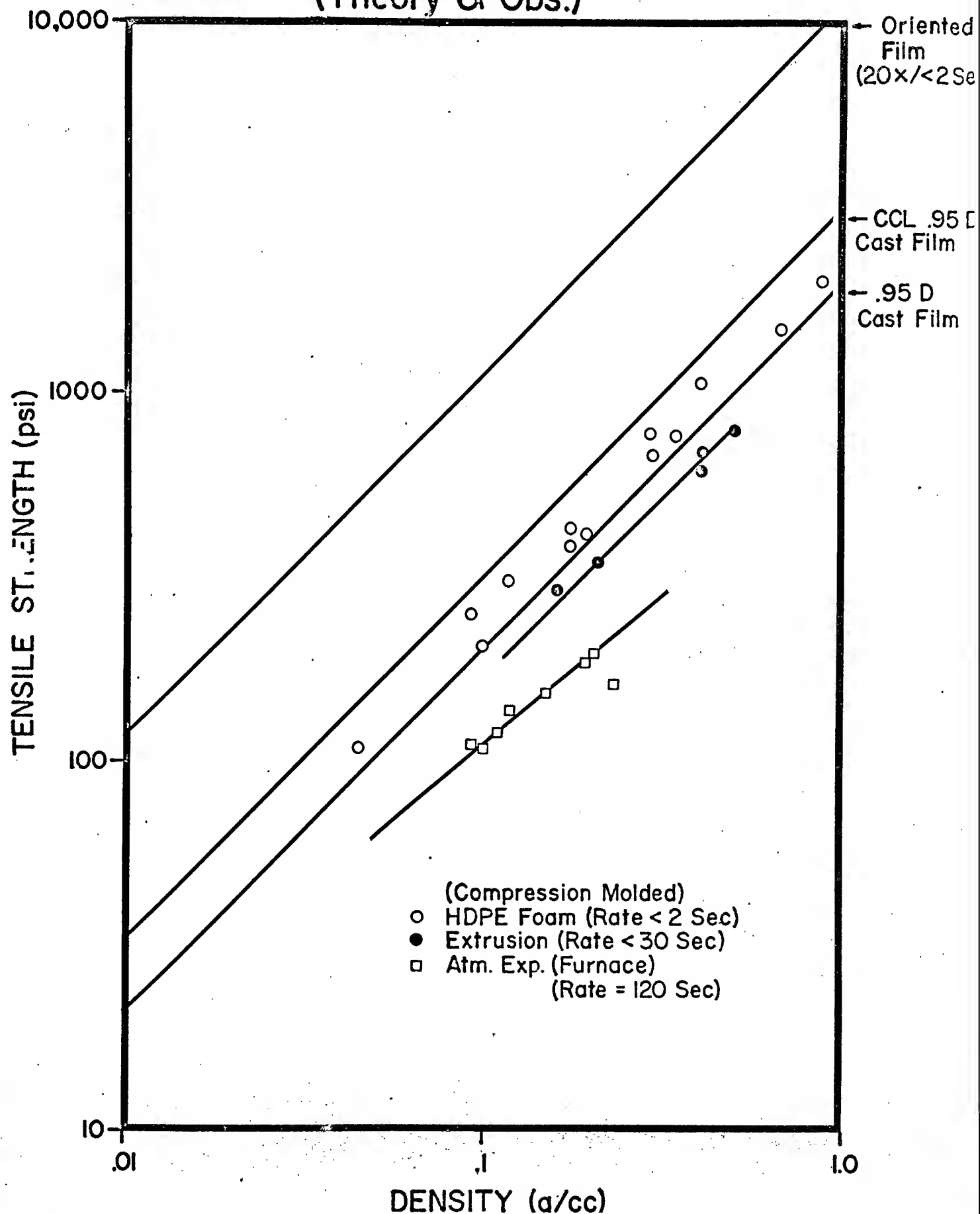


FIG. 16
 PROPERTIES OF POLYSTYRENE FOAMS
 (Theory & Obs.)

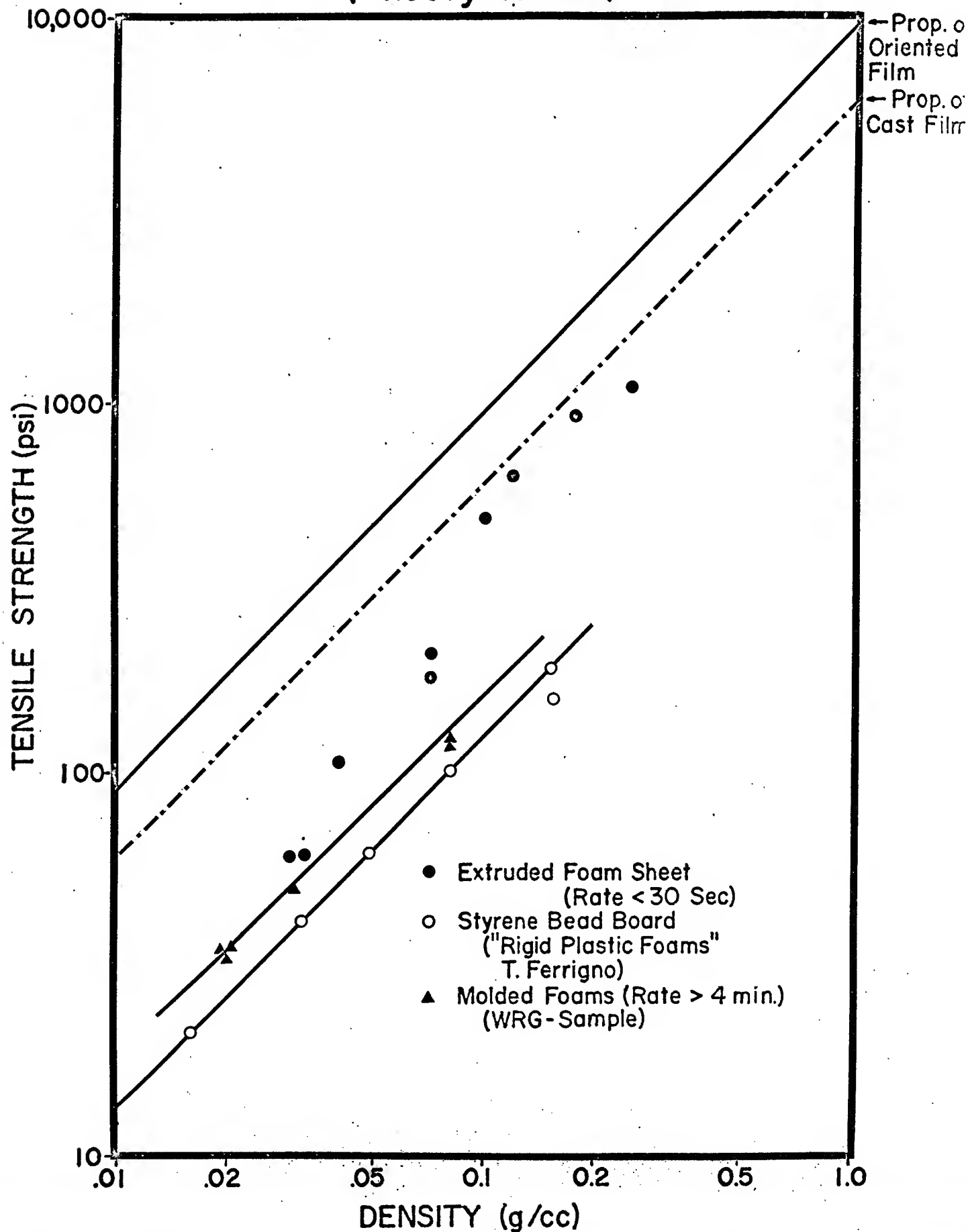


FIG. 17
RECOVERY VS. TEMP. OF EXPANSIONS

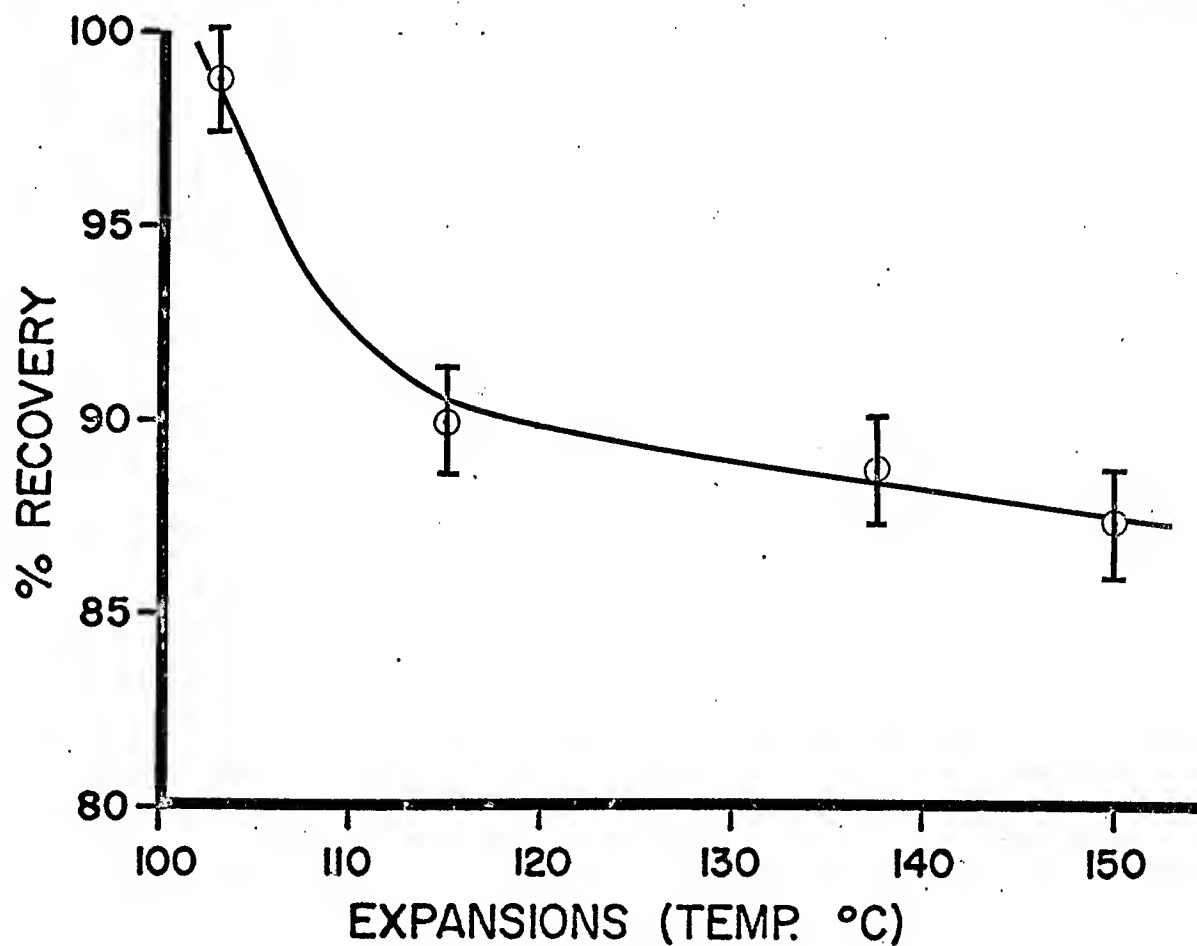


FIG. 18
RELAXATION OF ORIENTED FILM

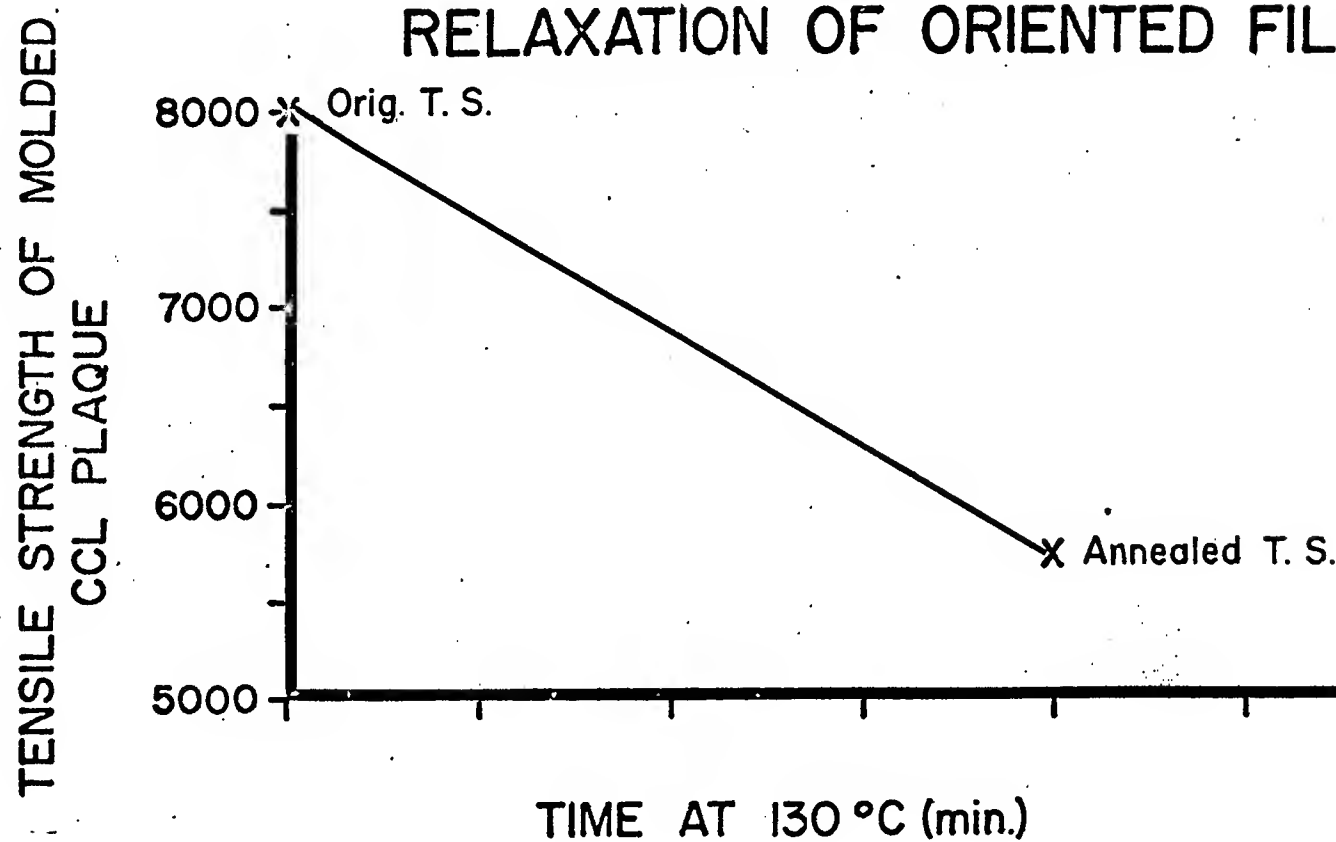


FIG. 19

THEORETICAL & OBSERVED FOAM PROPERTIES

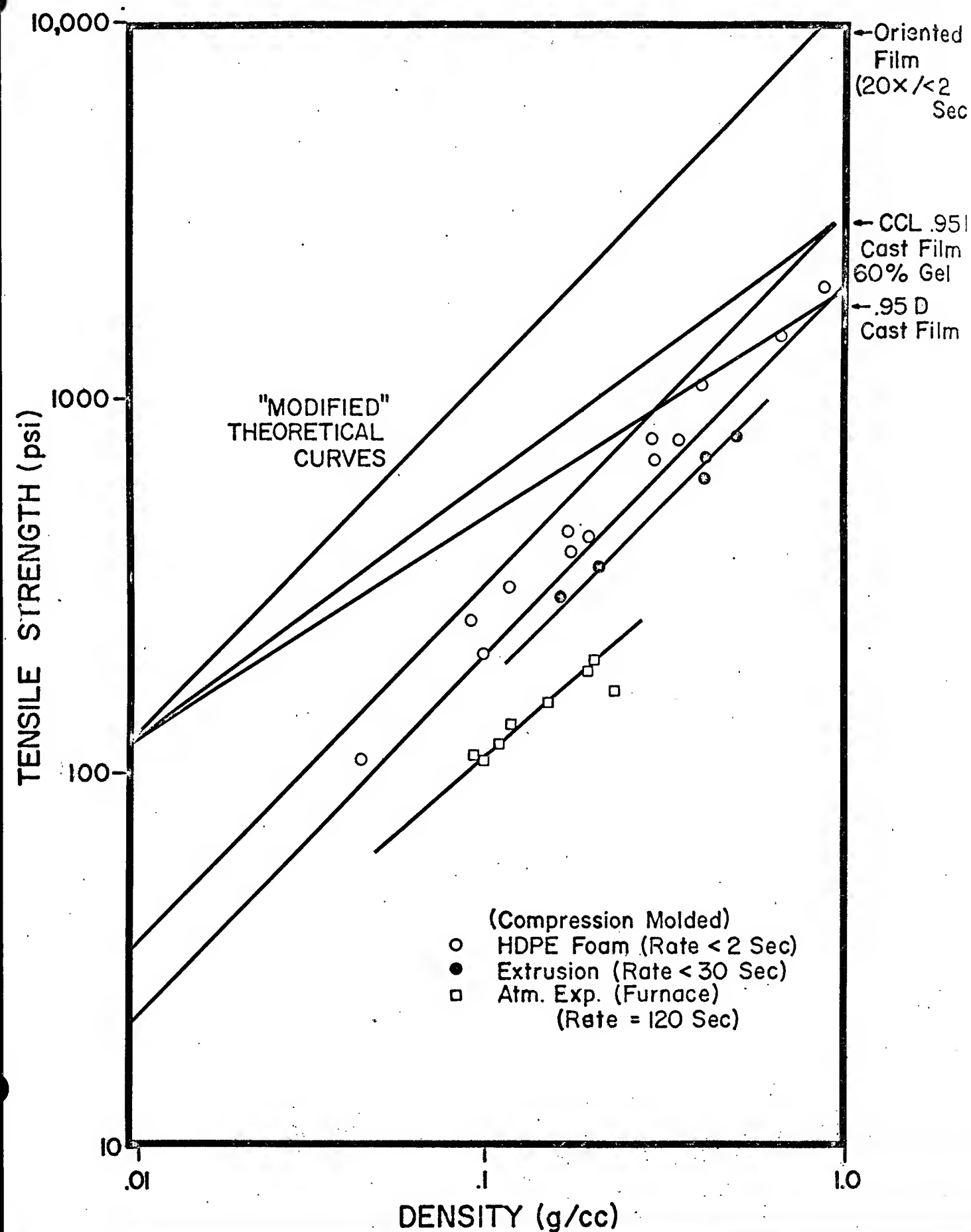


FIG. 20

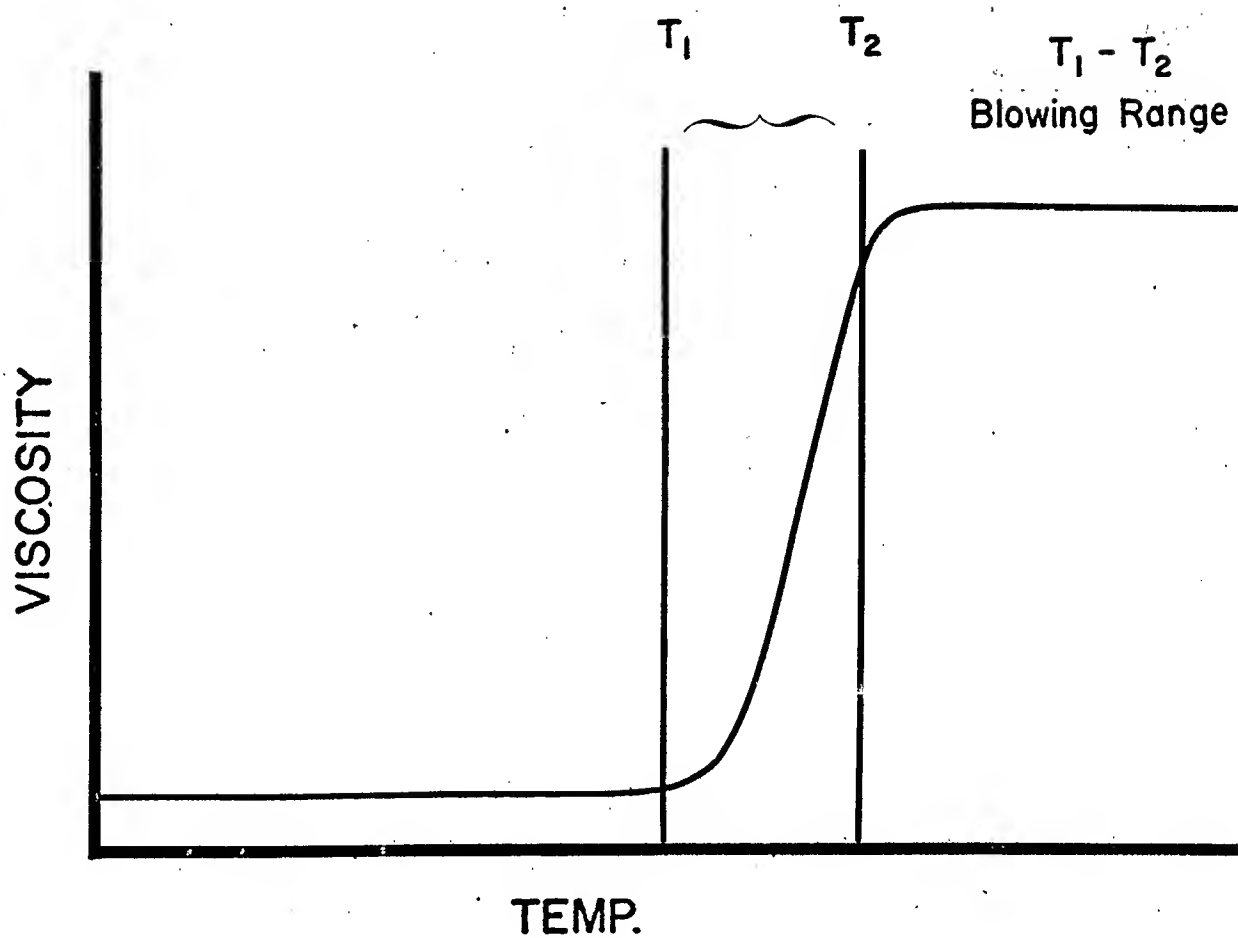
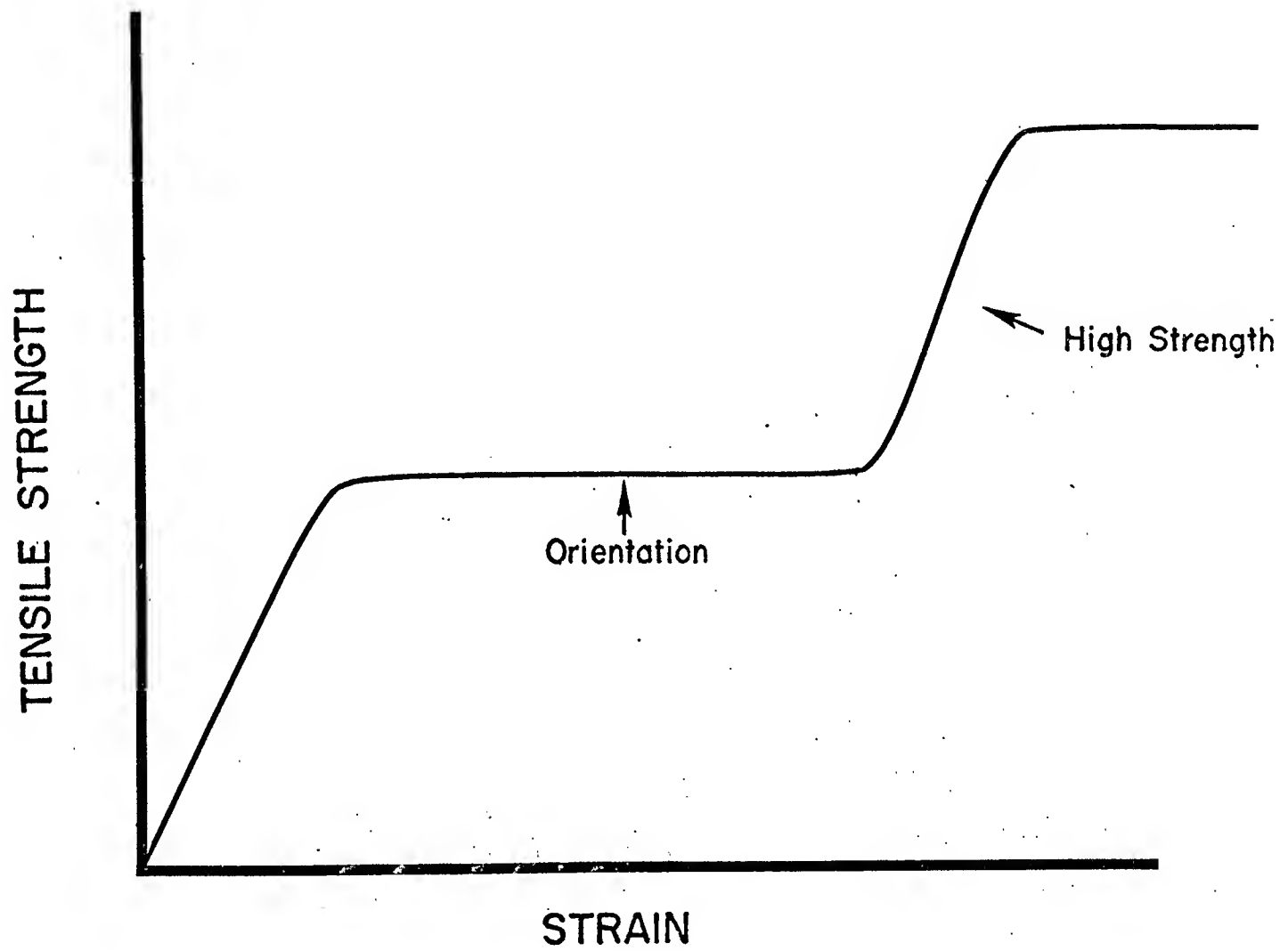


FIG. 21



10214-10

RIGID CELLULAR PVC

By

F. J. Wherley

The B. F. Goodrich Company

PVC has been converted to a rigid cellular product by several rather ingenious techniques. In order for you to understand more readily why such methods were employed I'd first like to touch on the processing characteristics of the unblown polymer.

PVC was first polymerized about a century ago but remained little more than a curiosity until the 1930's. Up to that decade, vinyl chloride was bulk-polymerized by exposure to sunlight. The chunks of polymer produced were brittle and intractable. If you tried to melt and mold it, it decomposed. Three developments then helped make PVC useful. Plasticizers were discovered which converted the intractable polymer into a rubbery material which could be worked at moderate temperatures on rubber processing equipment. Stabilizers were found which retarded the decomposition of PVC at these temperatures. And emulsion polymerization systems were developed which could produce commercial quantities of polymer as a fine powder.

Production of flexible PVC products then increased rapidly in this country during the 1940's under the press of wartime shortages. Rigid PVC was a more difficult problem. In Europe shortages of metals and cellulose forced the development of some rigid PVC products by compression molding, calendering and some extrusion.

PVC of low molecular weight was required or the polymer was degraded considerably. It wasn't until the late 40's and early 50's that lubricants, processing aids and new equipment were developed that made possible high quality rigid PVC by extrusion and, later, injection molding.

The lubricants are generally waxes or fatty acid esters which are incompatible with PVC. They lubricate the metal surfaces of the processing equipment. Perhaps more importantly they appear to coat the individual particles of PVC powder and keep them from uniting completely into a homogeneous mass. This kept the viscosity and flow resistance down so that the PVC could be processed at less than 380°F. where the stabilizers available were adequate. Processing pressures had to be twice as high as that required for other thermoplastics. The processing aids are partially-compatible resins which are added to help bond everything together in the finished product.

If this rigid product is fractured rapidly, the fractured surface reveals the boundaries of the initial PVC powder particles. This hasn't been a serious handicap to the utility of rigid PVC, but the film-forming characteristics needed to produce a thin-walled foam certainly aren't in this picture. Unlike polystyrene and polyethylene, PVC does not form a true melt under these normal processing conditions.

Only during the past few years, with more sophisticated, mixed stabilizer systems, more stable PVC and extruders with high-intensity tips have we been able to heat PVC to 420-440°C. for a brief period without decomposition. A true melt has finally been obtained, with PVC of fairly high molecular weight. And it is now possible to extrude thin tough blown film.

The effects of molecular weight on PVC properties and viscosity are shown schematically in Figure 1. As the molecular weight is increased properties improve and the viscosity increases, reducing processability. Mechanical properties such as strength and modulus tend to level off near molecular weights which can now be extruded and somewhat above molecular weights which can be injection molded. Elongation continues to improve with even higher molecular weights. In order to make decent fibers, films and, by analogy, foams, PVC of the highest possible molecular weight is used. This is necessary in order to obtain cohesiveness of the polymer during processing, and for the product to be able to elongate during impact and hence be tough. If the molecular weight is too low the polymer may pull apart during processing and the product will be brittle. If molecular weight is too high processing to the desired product won't be possible.

The other aspect of the problem of using PVC with a high molecular weight is shown schematically in Figure 2. As temperature is increased

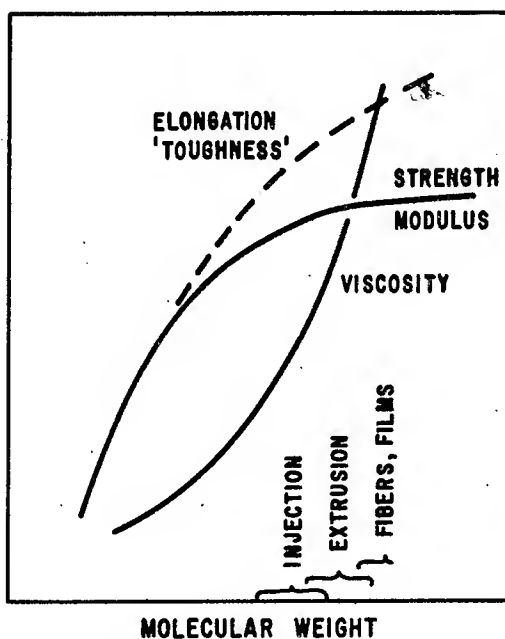


Fig.1. EFFECT OF MOLECULAR WEIGHT ON PROPERTIES AND VISCOSITY OF PVC

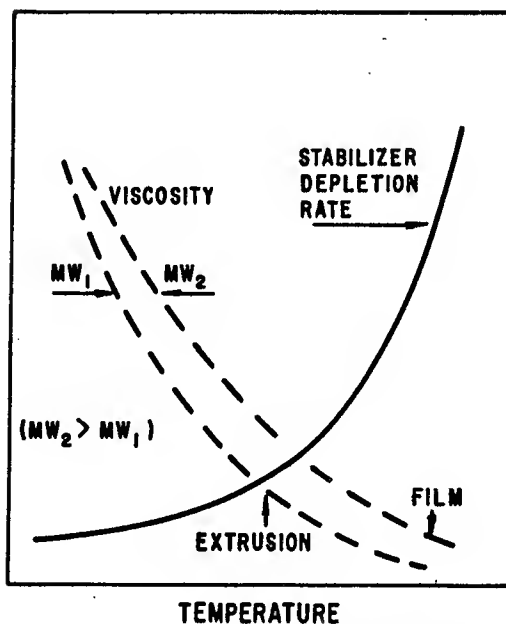


Fig.2. EFFECT OF TEMPERATURE ON VISCOSITY AND STABILITY OF PVC

to bring the polymer viscosity down to that required by the process, stabilizer depletion rate increases and the period during which the polymer is stable shortens. Extrusions with thick cross sections can be made from a fairly viscous stock, which can be attained with a standard PVC at moderate temperatures where the stability period is fairly long. Films require a higher MW PVC and a lower viscosity. So considerably higher temperatures must be used and the compound loses its stability rapidly. Heating of the PVC compound and cooling of the extruded film must be done quickly, as indicated. Good descriptions of PVC technology with many references may be found in two recent publications.^{1,2}

Given these properties of PVC how has it been converted to cellular products and what are their properties and uses?

Table I outlines the techniques which have been devised to prepare rigid cellular PVC products. The general procedure is to convert the PVC to a plastic mass containing the blowing agent, expand the mass during or after extrusion or molding and then deplasticize to rigidify the foam. Nearly all rigid cellular PVC materials are made with a temporary plasticizer which, after cellurization, is either evaporated or converted to a rigid product. There has been some success with other techniques which I'll describe first.

TABLE I

PROCESSES FOR RIGID CELLULAR PVC

<u>Plasticization with</u>	<u>Deplasticization by</u>
1. <u>Heat</u>	
(a) high temperature plasticizers	Cooling
(b) high melting plasticizers	
2. <u>Temporary Plasticizers</u>	
(a) Volatile	Evaporation
(b) Reactive	
1. Monomers	Polymerization
2. Anhydrides	Reaction with H ₂ O
3. Isocyanates	Reaction with H ₂ O

The most recent accomplishment has been the preparation of extruded high density expanded PVC without the aid of 'plasticizers'. A typical general formulation is shown in Table II.

TABLE II

RIGID PVC COMPOUND

PVC	100
Process Aid	10
Impact Modifier	10
Stabilizer	3
Lubricant	1
Azodicarbonamide	0.2-1.0

The 25 parts of additives modify the fluidity of the melt but are not plasticizers for the PVC. Several recent publications describe the production of high-density cellular PVC.³⁻⁶ The examples

described are plasticized compounds, but much of the process requirements listed hold for rigid products.

The compound can be made by powder mixing all ingredients, and tableting if desired, or it can be prepared by mill mixing and granulating all ingredients except the blowing agent which is then tumble-mixed with the granules.

The extruder should have a L/D of 15 to 20:1, a compression ratio of 1.25 to 2.5:1, and a decreasing flight depth and constant pitch. This fairly standard PVC screw can be used to make plasticized cellular vinyl which is processed at about 360°F.. For rigid formulations the exit end of the screw is modified to insure streamline flow with no dead or hot spots, and to shear the melt intensely to momentarily produce temperatures of around 430°F..

The melt expands very shortly after leaving the die. The rate of expansion is rapid and high shearing forces are exerted on the die edge. To insure smooth skins and no tearing, the extrudate should be removed rapidly from the die to prevent too much expansion close to the die. Expansion should be finished within several inches. The die should be operated about 50°F. cooler than the stock temperature and should be designed with a constant taper and no land. The cooler die will prevent bubble formation within the skin and increase its strength, reducing the chances of tearing.

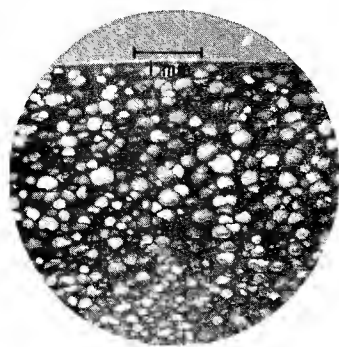
The dense unblown skin of a typical extrudate is shown in Figure 3(a). The mechanical properties of samples with skins are shown in Figure 4 and those of a skin-free section are listed in Table III. Calculations for a simple cantilever beam using the moduli of Table III show that equivalent stiffness can be obtained with 10% less material when the cellular PVC is used. The integral sandwich structure obtained with the normal skins intact, saves a bit more weight.

TABLE III

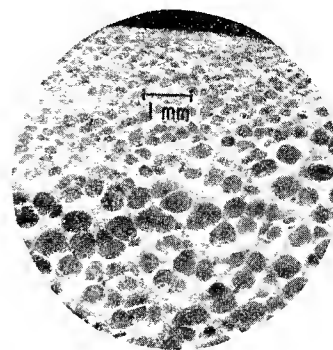
PHYSICAL PROPERTIES OF HIGH DENSITY EXPANDED PVC

	<u>Blown</u>	<u>Unblown</u>
Density (# / ft ³)	50	87
Hardness(Durometer D)	50	80
Tensile Strength (psi)	1,500	7,300
Elongation (%)	14	15
Flexural Yield Strength (psi)	2,600	14,500
Notched Izod (ft # /in)	0.77	0.80
Modulus of Elasticity (psi)	90,000	410,000
Heat Distort. Temp. at 264 psi (°F.)	133	158
Thermal Cond. (Btu/hr/ft ² /(°F. /in))	.80	1.4
Water Immersion (% Pickup)	2.0	0.01

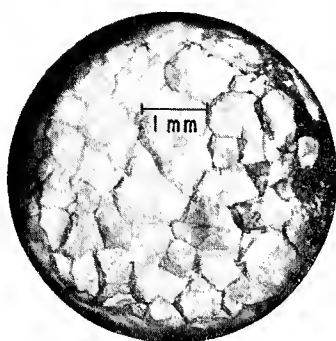
The additional thickness and lower thermal conductivity reduces the heat transfer rate to about 30% that of an unblown section of equivalent stiffness. In other respects the properties are lowered, and the blowing gas should be considered more as a filler which can be added to reduce the cost/volume. Extruded shapes in the form of pipe, board, window sash, rods, etc. are readily made.



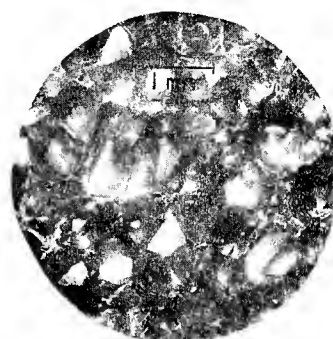
(a) Extruded High Density



(b) Fishfloat Section



(c) Dynazell Cross Section



(d) PVC-NCO Foam

FIGURE 3 RIGID CELLULAR PVC

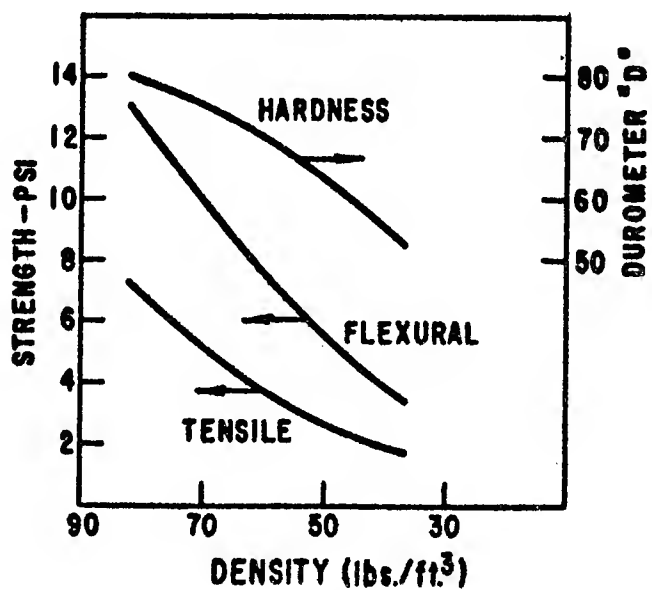


FIGURE 4 EXTRUDED RIGID CELLULAR
PVC-MECHANICAL PROPERTIES

Hi Temperature Plasticizer

Another technique has been described for making a rigid expanded PVC.⁶ Chlordiphenyl ether (65% Cl) is a plasticizer for PVC at elevated temperatures and is not a plasticizer at room temperature. In a cellular PVC product, 20 parts increases the softening temperature, at low stress, about 30°C. over that of the same compound without this additive. Products weighing 6-8 lbs/ft³ have been made with 17 parts of azo-di-isobutyronitrile (AIBN) or 26 parts of diphenyl sulphone-3,3-disulphhydrazide. The tetramethyl succinonitrile by-product of AIBN is a plasticizer for PVC and gives a product with a softening temperature of 80°C. compared with 100°C. when the latter blowing agent is used. Because AIBN can generate this toxic by-product,⁷ it is not widely used in this country as a blowing agent.

Polyketone resins softening above 75°C, have also been suggested⁸ as plasticizers for PVC. Below the softening point of the resin the PVC product is rigid.

Temporary Plasticizers

Practically all present commercial production of rigid cellular PVC is made by processes using some form of temporary plasticizer. Much art is involved, each manufacturer orchestrating his own variations of the basic processes. Combinations of several of the techniques listed in Table I may be employed. Consequently manufacturing

procedures, derived mainly from the patent literature, and discussed in the following sections, may not be practiced commercially exactly as described.

Volatile Solvent

A wide range of solvents have been suggested for plasticizing PVC and also for providing some of the blowing power for making molded expanded products.⁹ A few of the solvents listed are acetone, trichloroethylene, dimethyl ether, dioxane, toluene, methyl chloride, tetrachlorethane, and ethyl chloride.

The method of making cellular PVC by molding is sometimes referred to as the double-blow process. The origin of the name will become apparent from the following description. The powder components of a recipe (PVC, stabilizer, N₂ - release blowing agent) are first thoroughly blended in a powder mixer or a ball mill. The PVC is a fine paste type powder variously characterized as having a 'high melting temperature' or a reduced viscosity of 0.5 to 2.0. From 50 to 150 parts of the volatile solvents are mixed with the powders in a mixer which can handle the paste or dough produced. In some cases the N₂ blowing agent is reduced or eliminated, and a non-plasticizing volatile liquid such as naphtha or cold propane is dissolved in the solvent to serve as the blowing agent. The mixture is charged to a high pressure mold and heated to 200-350°F. to gel the PVC and

generate the N_2 . Pressures of 2-3000 psi are usually developed. The hot gelled biscuit may be nucleated at this point by increasing the mold volume 30% before cooling, or the fused biscuit is just cooled and nucleation occurs on demolding.

The first blow occurs when the biscuit is demolded and expands to 1.2-2 times the mold dimensions. Further expansion occurs when the biscuit is placed in an oven at 150-250°F. for a period of an hour or as long as several days. During the evaporation of the solvent, the product may grow to 3 times the mold dimensions and then finally shrink back to a final size 2.5 times the mold size. During this time, stresses are relieved and the gas in the cells equilibrates with air to give a stable product. In spite of these dimensional changes, the original mold shape is retained and the finished size can be reproduced fairly closely.

In another version of the technique, a fused non-expanded slab containing volatile plasticizer, but no blowing agent, is exposed to a gas such as ethane at about 500 psi for several days. When expanded in an oven, foams with exceptionally fine pores (2 microns) are obtained.

The products made in this manner have a non porous skin and are used for their insulating, packaging or flotation characteristics. Millions of fishing floats from rigid expanded PVC are in commercial

use throughout the world.¹⁰ The buoyancy characteristics of a typical float with a density of 7 lbs/ft³ are shown in Table IV.

TABLE IV

<u>Depth (feet)</u>	<u>Buoyancy #/ft³</u>
50	55
200	55
250	54
300	23
400	17

A float section from near the skin is shown in Figure 3(b).

Volatile plasticizers have also been used to make extruded cellular vinyl.¹¹ A piece of equipment is described, in one method, in which granules of PVC are soaked in a pressurized pool of heated liquid chlorofluorocarbon until the desired amount of the volatile liquid is absorbed. The confined granules are then conveyed from the bottom of the treating tank to the screw of an extruder which produces the expanded product.

In a variation of this technique a volatile solvent, such as acetone, is injected into the working zone of an extruder and uniformly dispersed in the PVC as the mix is carried to the die. In this process 1000g PVC, with a Kvalue of 70, containing 2% Pb Stearate may be mixed with 400cc. of acetone at a barrel temperature of 160°C. At this temperature the acetone will have a vapor pressure of about 30 atmospheres. The pressure is

maintained high enough to prevent expansion until the mixture leaves the extruder die. The exit speed of the extruded, expanding noodle may be more than 10 ft/sec. The density of the strand can be as low as 1 lbs/ft³ -which must be about the lightest PVC foam made. A cross section of such an extrudate is shown in Figure 3(c). The individual strands may be 100% closed cell to soapy water, and 80% closed cell as measured by air displacement. If a number of strands are ejected simultaneously into a common receptacle, they will adhere together while still hot. And consolidated blocks weighing less than 2 lbs/ft³ can be formed. These blocks of 'Dynazell' are now under development by Dynamit Nobel.

The compressive strength of the rather resilient block will be about 3 psi at 10% deflection, the thermal conductivity 0.26 Btu/hr/ft²/(°F/in). The sound absorption properties of a block of Dynazell are shown in Figure 5. This material is being evaluated as a subway tunnel lining to reduce sound transmission where trains run under apartment buildings. It is also being tested as a means for reducing the sound transmission from upper apartments to those below. A thin concrete floor is 'floated' on slabs of PVC which in turn rest on the structural subfloor. The rather resilient foam decouples the floor above from the ceiling below, producing the required decible reduction.

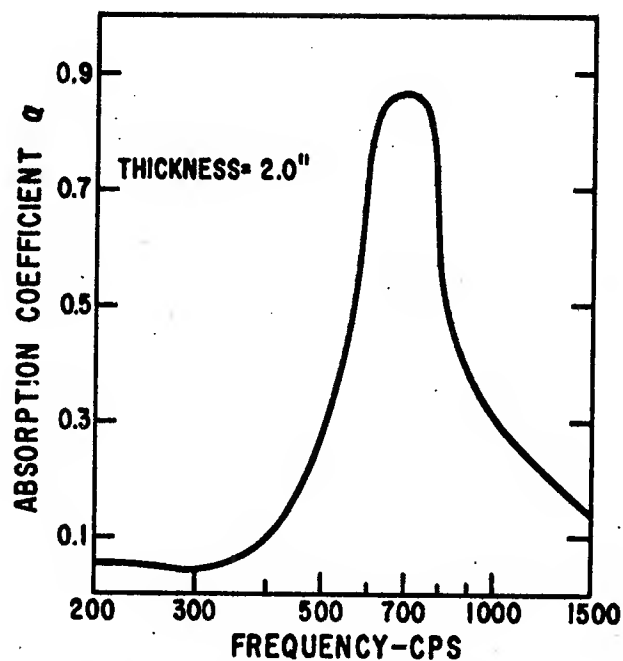


Figure 5. SOUND ABSORPTION PROPERTIES OF DYNAZELL

Monomers

Monomers have also been used as temporary plasticizers for making cellular PVC by the double blow process.¹² Compatible monomers that are effective include styrene, methacrylates, acrylates, acrylonitrile and vinyl acetate. In some cases an inhibitor such as hydroquinone is included to prevent too much polymerization during molding and before blowing. When the foamed product is then heated, the monomers are reported to polymerize faster than a volatile solvent can be removed by comparable heating. In my

own experience, just as it is difficult to evaporate the last few per cent of a volatile solvent from a foam, the complete polymerization of some of these monomers can be quite difficult. The new polymer formed becomes a part of, and can improve the properties of the foam.

A volatile plasticizer may be included with the monomer to help attain even lower density. A typical recipe is listed in Table V. In this example, the first three ingredients are ball milled for 1 1/2 hours, then the remaining ingredients added to the powder in an internal mixer. The mixture is molded 12 min. at 2000 psi and 164°C., coded and demolded. The resultant slab is expanded at 175°C. for 30 min. then heated at 200°F. until hard.

TABLE V

PVC	100
AIBN	15
Pb Stearate	15
Styrene	45
Acetone	45
Hydroquinone	5

Final density is 3.4 lbs/ft³.

Epoxides

Foams can also be prepared by the two stage process using an epoxy as the temporary plasticizer.¹³ For example, a

homogeneous paste with a viscosity of 10,000 cps is obtained by mixing on a 3-roll mill 100 parts of a paste-resin PVC, 20 of AIBN, 2.5 of Pb Stearate, 50 of epoxy and 50 of a liquid eutectic mixture of 75% hexahydrophthalic anhydride + 25% tetrahydrophthalic anhydride. This paste is charged to a 0.3 inch deep mold cavity preheated to 80°C., then heated under pressure to 150°C. for 5 minutes, and cooled rapidly to room temperature to prevent excessive cure of the epoxy. The sample expands 4-5 fold when demolded. On further heating to 100°C. for 16 hours the foam expands 3-4 times the demolded volume to a final density of 5 lbs/ft³ and the epoxy sets up. Though the product is still soft at 100°C., at room temperature it has a compressive strength of 110 psi. Cell diameter is 0.3 mm.

The densities obtained with various amounts of blowing agent are shown in Table VI. These densities are typical for many foam systems where the blowing agent is the only source of expansion.

TABLE VI

<u>Parts AIBN/200 Resin</u>	<u>Density</u>
0	80 #/ft ³
2.5	43
5	19
10	12
20	5.0
30	3.8
40	2.5
60	1.9

If the epoxy system content is doubled, paste viscosity drops to 3000 cps and cell diameter increases to 1 mm. If it's cut in half the viscosity increases to 30,000 cps and the cell size drops to 0.1 mm. This relationship is typical for foam systems-- the greater the viscosity of the media in which nucleation can occur rapidly (as during demolding), the smaller is the cell size obtained.

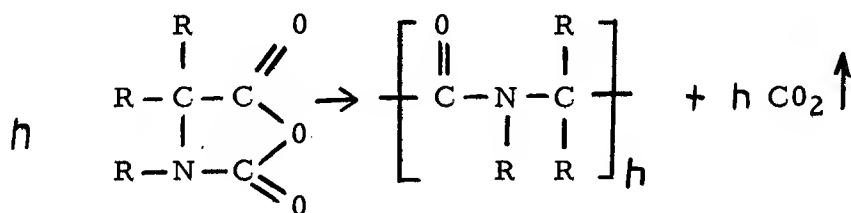
Anhydrides^{14(a-c)}

Phthalic anhydride and maleic anhydride are interesting plasticizers for PVC which can be converted to non-plasticizing acids by hydrolysis. ^(a) The double-blow process is used and after expanding the demolded slab for 20 minutes at 115°C., the rather soft foam is allowed to normalize for a day. Then a new process step enters the picture for the first time. The foam is heated at 90°C. and 100% relative humidity for three hours. As water diffuses into the foam, the anhydrides are converted to acids which are not plasticizers for PVC.

In a variation of this technique, ^(b) inorganic carbonates or peroxides are included with the anhydride. After exposure to water the acids formed react with the inorganics to produce additional gas for expansion. These secondary gas-forming reactions and the additional expansion can be effected, after water treatment, in a separate step under vacuum at 100°C. to attain even lower densities.

In both of these processes using anhydrides the formulations are powders and include a nitrogen blowing agent.

Aminoacid anhydrides^(c) have also been proposed to serve as plasticizer, blowing agent and reinforcing polymer in PVC foams. When a mixture of PVC and the anhydride is heated to 125-200°C. the following reaction occurs.



The anhydride plasticizes the PVC, CO₂ expands the composition and the linear polyamide reinforces the cellular structure.

Isocyanate-PVC Foams

Now that we've covered a number of proposed and commercial techniques for making a rigid cellular PVC, the process using isocyanates as temporary plasticizers may not seem quite so complex and unusual. Foams made in this manner have reached considerable commercial significance in Europe. Licenses to practice the process in this country have recently been issued to B. F. Goodrich, and Johns Manville by Kléber-Colombes Polyplastique.¹⁵ These are the only low-density PVC foams made whose properties bring

them into competition with polyurethane and polystyrene foams where both strength and insulation are a factor.

The patents ^{16(a-j)} covering this process begin with the original concept of Carpentier, (a) issued in this country in 1951. In recent years the process has been greatly refined and modified, largely through the efforts of Yvan Landler, Pierre Lebel and associates at Kléber-Colombes.

The process is basically the double-blow process modified by exposure of the demolded material to water in the final step. As outlined by Carpentier, the ingredients (Table VII, (a)), which are

TABLE VII

Typical NCO-PVC Foam Recipes

	15(a)	(b)	(c)	(d)
PVC	100	100	100	100
Toluene Diisocyanate	45	35	59	53
AIBN	13	2.9	20	10
Tricresyl Phosphate	28	-	-	-
Alphaphenylindol	1	-	-	-
Phthalic Anhydride	-	41	-	-
Calcium Carbonate	-	6.8	-	-
Dutrex V 10	-	10	-	-
Hard Asphalt 155/0	-	-	27	-
Maleic Anhydride	-	-	-	20
Styrene	-	-	-	10
Foam Density(# /ft ³)	3.4	3.1	2.5	1.9

free of water, are thoroughly mixed, then molded at 5000 psi and 175°C. for 10 minutes. The slab is cooled under pressure to room temperature, demolded, then heated to 110°C. for 30 minutes. The density of the resultant soft foam was 7 lbs/ft³ or about what would be expected from the amount of AIBN used. This foam, after resting 24 hours, was heated at 78°C. and 100% relative humidity for 2 hours to produce the final hard product with a density of 3.4 lbs/ft³. The polyurea products, formed by the reaction of water with the toluene diisocyanate (TDI) reinforce the cellular product.

The system has been modified to include phthalic anhydride in place of part of the isocyanate as the temporary plasticizer, and CaCO₃ in place of part of the AIBN. ^(b) The permanent primary plasticizer was also replaced with a lesser amount of a secondary plasticizer. The mechanical properties of the foams produced are good, but they cannot be expanded to less than 2.5 lbs/ft³ and their thermal dimensional stability is low. Shrinkage may be 50% or more after one week at 90°C.

Temperature resistance has been increased somewhat by using a high-melting asphalt ^(c) as the only plasticizer besides TDI. The asphalt helps to produce a stress-free foam during the latter stages of water treatment when the foam is still trying to

expand and the plasticizing isocyanate has disappeared. The foam remains rigid until the softening temperature of the asphalt is exceeded.

Isocyanate + Monomers

Foams with densities as low as 1.5 lbs/ft³ and with a much improved temperature resistance are obtained with the most recent formulations. (d) Phthalic anhydride and permanent plasticizers are eliminated, and an ethylenic anhydride such as maleic anhydride is added together with a vinylidenic monomer such as styrene, vinyl acetate, acrylonitrile and the like. An adduct of maleic anhydride and a diene may also be added. (j) A small amount of catalyst such as AIBN or a peroxide is included to induce polymerization of the monomers during the molding operation. From 5-30% of a saturated halogenated hydrocarbon can be included in the recipe (g) to aid in expansion and reduce the thermal conductivity of the foam.

The process is similar to that already described. The ingredients are mixed about 5 minutes in a Werner type internal mixer. The paste obtained is then molded under pressure at 175°C. for ten minutes. Because the polymerization exotherm is about 40 kcal per mole, fusion temperature is reached rapidly.

The fused 'prefoam' may be cooled before demolding or it can be demolded hot,^(h) Some process and product advantages accrue to this latter technique as shown in Table VIII.

TABLE VIII

Hot Demolding

<u>Demolding Temp(°C)</u>	<u>Demolded Density(#/ft³)</u>	<u>Mold Cycle Time(min)</u>	<u>Hot Water Expansion(hrs)</u>	<u>Final Density</u>
unblown	75			
25	64	60	6	4.9
50	56	53	5	4.7
100	27	42	3	3.4
150	16	34	1.5	2.5
175	rupture			

The mold cycle time is shortened because the press always remains hot. Water diffuses more rapidly into the pre-expanded slab and the faster reactions permit the foam to expand further before the surface becomes hardened. Foam slabs up to 6 inches thick can be made compared to about 4 inches maximum from a prefoam demolded cold. In addition the greater supersaturation of blowing gases and vapors in the hot, less-viscous prefoam produces a faster nucleation and smaller cells than obtained in a prefoam demolded cold.

The cell structure is fairly regular (Figure 3(d)) and the properties close to isotropic in the usual product. Another

modification⁽ⁱ⁾ in the molding technique is used to produce anisotropic foams. After fusion is completed the mold cavity is doubled in thickness before cooling to the desired demolding temperature. The compressive strength of the foam produced may be 30-40% greater in the direction of this nucleation operation than at right angles to it.

The demolded plastic foam may then be rested several hours before being placed in a steam chest or immersed in boiling water to effect the final expansion and hardening. If immersed in boiling water^(f) the material may be held in contact with a downward-facing molding surface by the hydrostatic thrust of the water, imparting a shape to the foam. Toward the end of the expansion period the bottom of the foam can be urged against a second molding surface located below the foam.

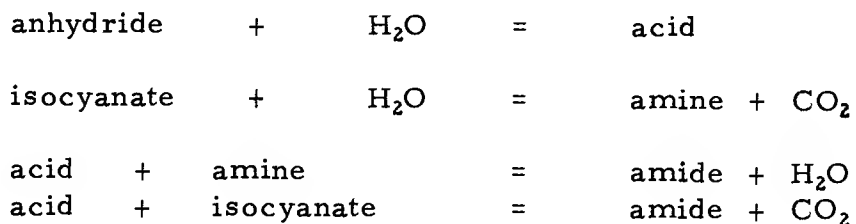
Cross-Linked Foam

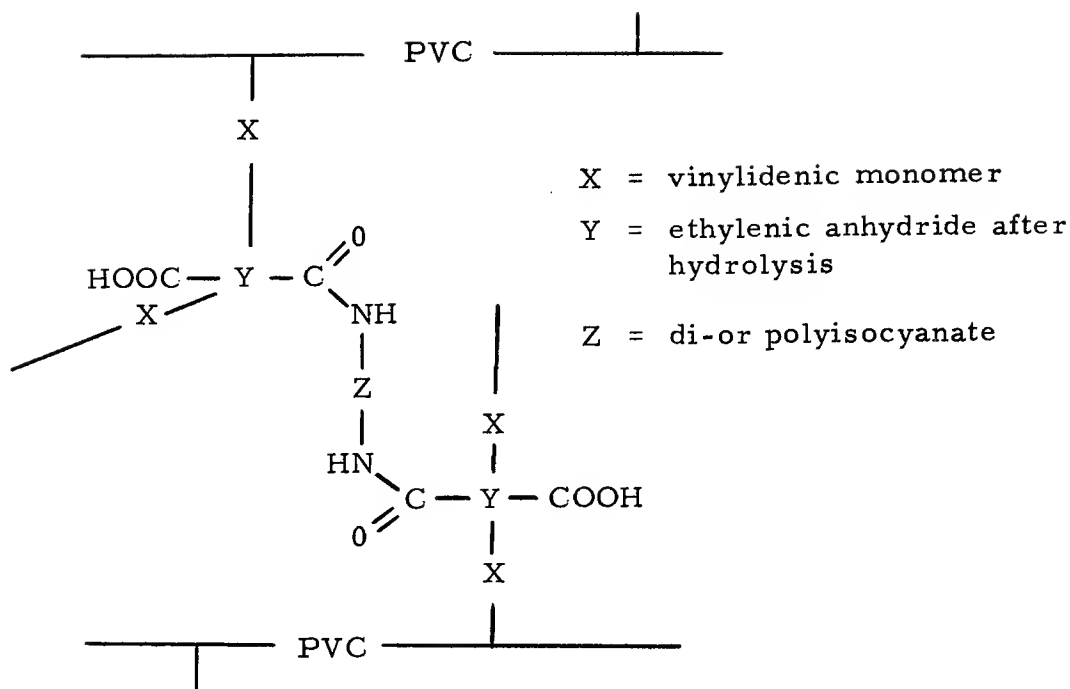
Following the molding operation, during which the monomers polymerize, the prefoam is still soluble in solvents for PVC such as dimethyl formamide (DMF). After water treatment, which causes interactions between isocyanate, anhydride and the water, the foam may be softened by DMF but is no longer soluble. In addition no PVC can be extracted from the foam. If the isocyanate or the maleic anhydride or the vinyl monomer is eliminated from the formulation,

the finished product, after water treatment, is still soluble in DMF.

If one of the required components is missing the foam will shrink 65% after 200 hours at 90°C.; if all are present shrinkage is only 5%.

The cross-linked structure is believed to arise in the following manner: During the molding operation the monomers copolymerize and graft to the PVC. If the copolymer formed is one that is soluble in water, and the prefoam is dissolved in DMF and precipitated repeatedly with water, the PVC fraction contains an irreducible part of the copolymer. During the water treatment the anhydride hydrolyzes. The acid formed reacts with isocyanate molecules, or with the amine formed from the reaction of isocyanate with water, to form amide bridges between the various macromolecules.





Extrusion

The above formulations can be modified slightly and extruded rather than molded in the first step of the process.^(e) In order to obtain a homogeneous cellular product, a nucleation aid such as a finely-divided silicate or charcoal is added. A polymerization catalyst such as a peroxide which doesn't generate gas is used rather than a catalyst like AIBN. The extrudate is forced through a cooling die and emerges as a non-cellular slab. Treatment of the slab with steam or hot water then generates the cellular product.

Mechanical Properties

For a better perspective of the properties of PVC-NCO foams⁽¹⁷⁾ I will compare them with those of polyurethane⁽¹⁷⁾ and polystyrene⁽¹⁸⁾

foam, where measurements by similar tests are available. The polyurethane foams reported were the best of those available in early 1965.

The comparative mechanical properties of a G-300 (Kléber-Colombes) series of PVC foams and polyurethane and polystyrene foams are shown in Figures 6-13. In general the strength properties of the PVC foams are the highest. The modulus properties of PVC and polystyrene are similar and considerably higher than polyurethane.

The mechanical properties of PVC-NCO foam at low temperatures are quite good.^{17,19} Figures 14 and 15 show the strength and modulus properties as a function of density at $-196^{\circ}\text{C}.$ And ultimate tensile strain, which is 2.5% at room temperature, is still 1.5% at even $-253^{\circ}\text{C}.$ Samples tested after immersion in liquid hydrogen for 5 hours are undamaged as indicated by before and after values of air permeability.

At elevated temperatures the PVC foams begin to soften. More than 70% of the room temperature shear strength is retained at $180^{\circ}\text{F}.$ Modulus retention can be from 25% to 80%, depending on formulation. Each type will consequently have its own maximum service temperature in load-bearing applications. The cross-linked varieties have the greater heat resistance as shown by their

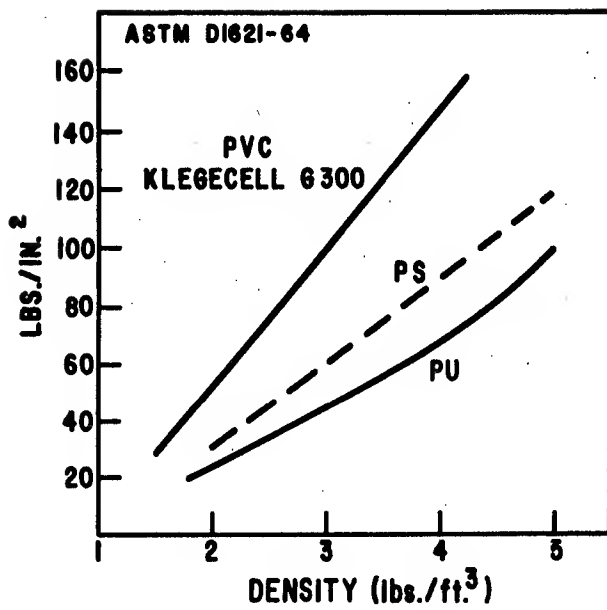


Figure 6. COMPRESSIVE STRENGTH vs. DENSITY

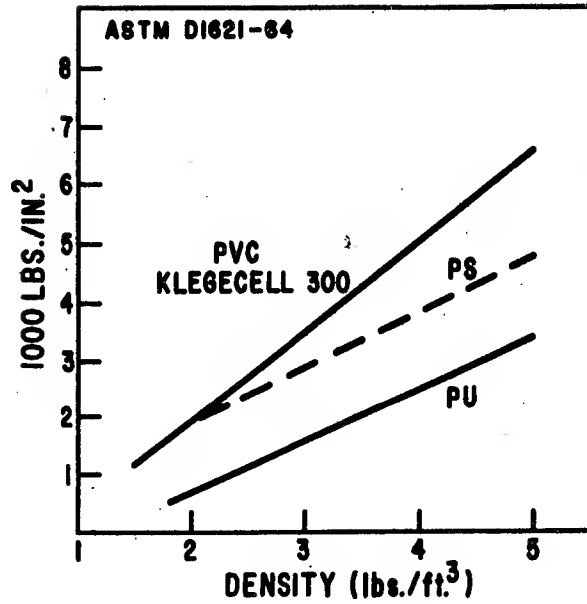


Figure 7. COMPRESSIVE MODULUS vs. DENSITY

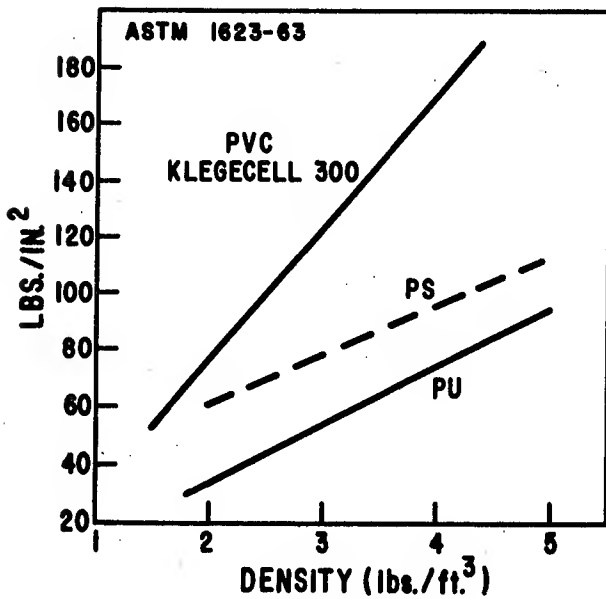


Figure 8. TENSILE STRENGTH vs. DENSITY

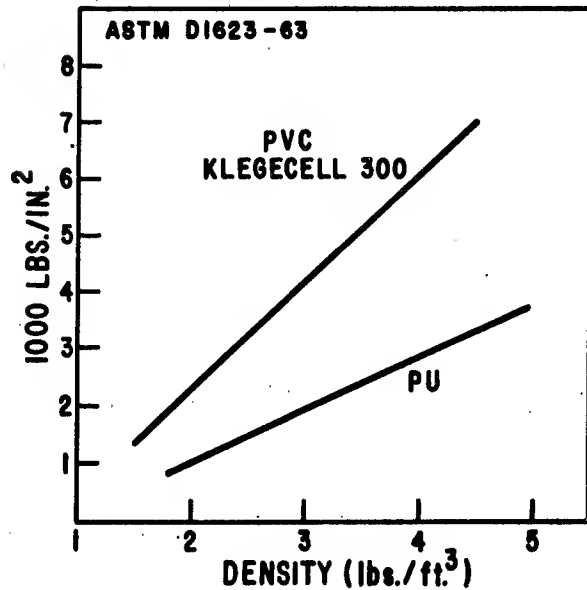


Figure 9. TENSILE MODULUS vs. DENSITY

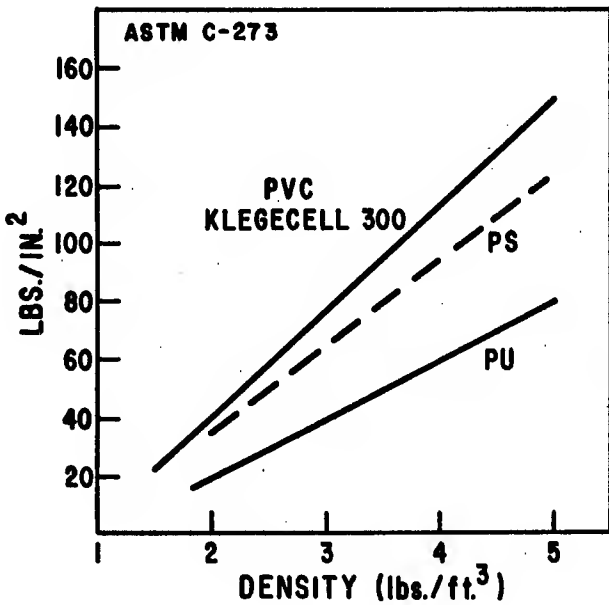


Figure 10. SHEAR STRENGTH vs. DENSITY

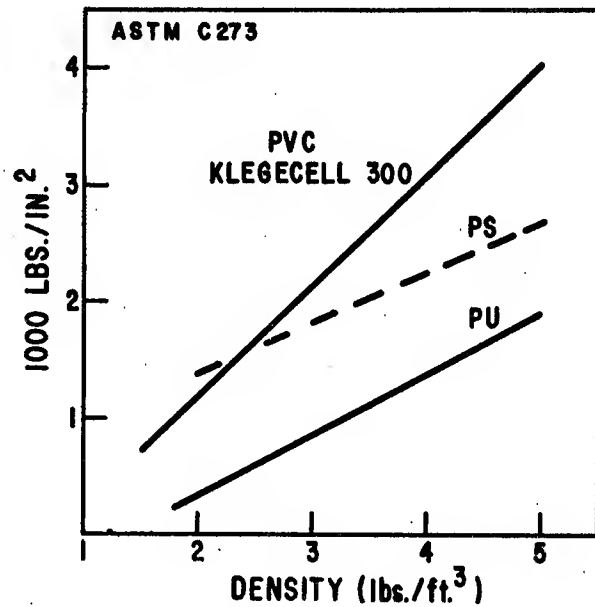


Figure 11. SHEAR MODULUS vs. DENSITY

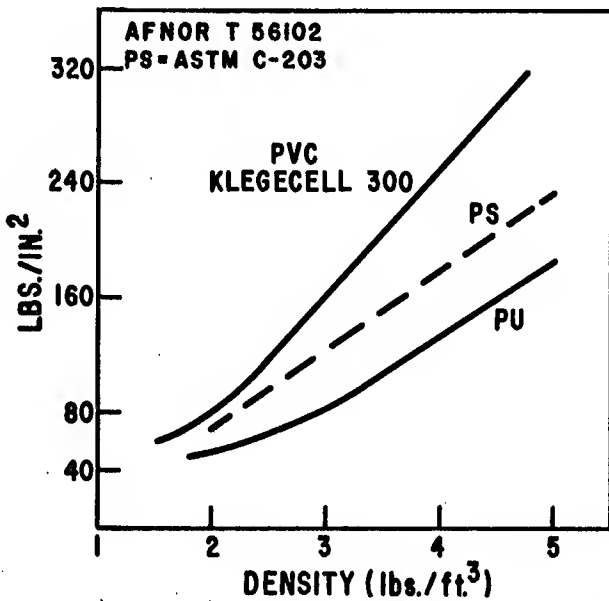


Figure 12. FLEXURAL STRENGTH vs. DENSITY

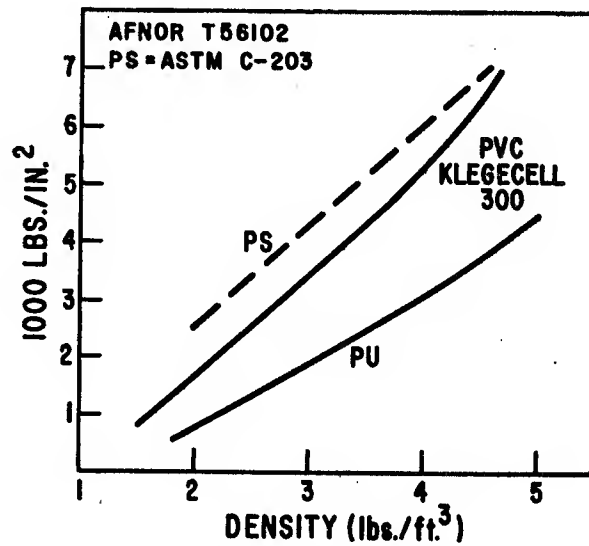


Figure 13. FLEXURAL MODULUS vs. DENSITY

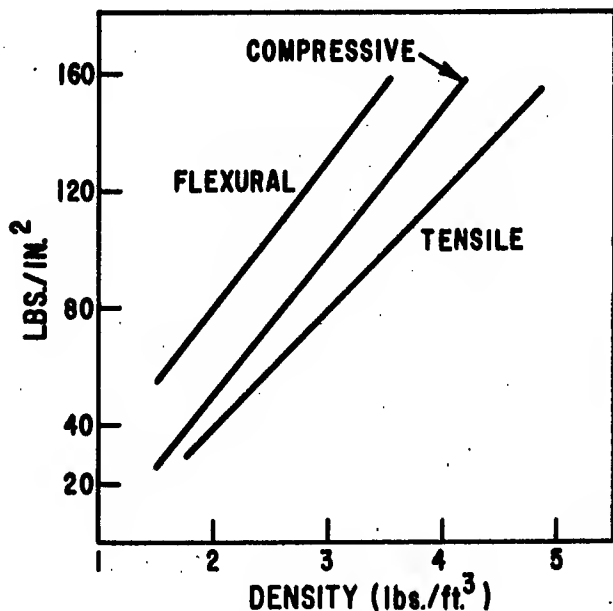


Figure 14. STRENGTH OF K300 PVC AT -196°C vs. DENSITY

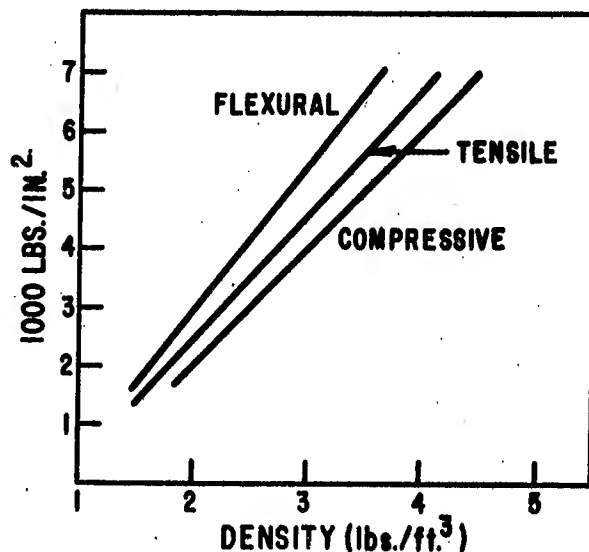


Figure 15. MODULUS OF K-300 PVC AT -196°C vs. DENSITY

dimensional stability. After 200 hours at 90°C. they will retain about 95% of their volume, while other formulations may shrink 50%.

We have to keep in mind, during this analysis, that rigid PVC-NCO foams can be made over a wide range of mechanical properties. Figure 16 shows the variety of shear stress-strain behaviors that can be obtained with different formulations of PVC foam in comparison with polystyrene and polyurethane. PVC foams can be made that break after a strain of only 5-6%, or that don't reach even a maximum shear strength until strained 35-40%. The PVC foam

behavior in shear is rather unique. It can exhibit a modulus and strength even greater than polystyrene and at the same time have the strain accommodation capability of a polyurethane.

The PVC foams are tough and relatively non-friable.⁽²⁰⁾ They are more comparable to polystyrene than to polyurethane in this property as indicated in Table IX.

TABLE IX

Density (lbs/ft ³)	<u>Charpy Impact*(ft/lb)</u>		<u>Abrasion Time**(sec)</u>	
	<u>1.5</u>	<u>2.5</u>	<u>1.5</u>	<u>2.5</u>
Polystyrene	.12	.20	600	1100
PVC	.10	.17	470	860
Polyurethane	.05	.07	70	120

* sample 0.5 x 0.5"

** Time to grind down 1" of 3/4 x 3/4" block against #1 Emery (200 g wt) on DuPont type abrader.

Fatigue Resistance

Sandwich panels made with PVC foam have good resistance to fatigue loading⁽²¹⁾ as shown in Figure 17. The panel tested was made of a 2 inch thickness of 3 lbs/ft³ foam faced with aluminum skins .038 in. thick. A rotating cam caused the beam to deflect 0.16 in. at the center of the span at a frequency of 15 cycles/second. After 50 hours the panel was tested to half its original ultimate

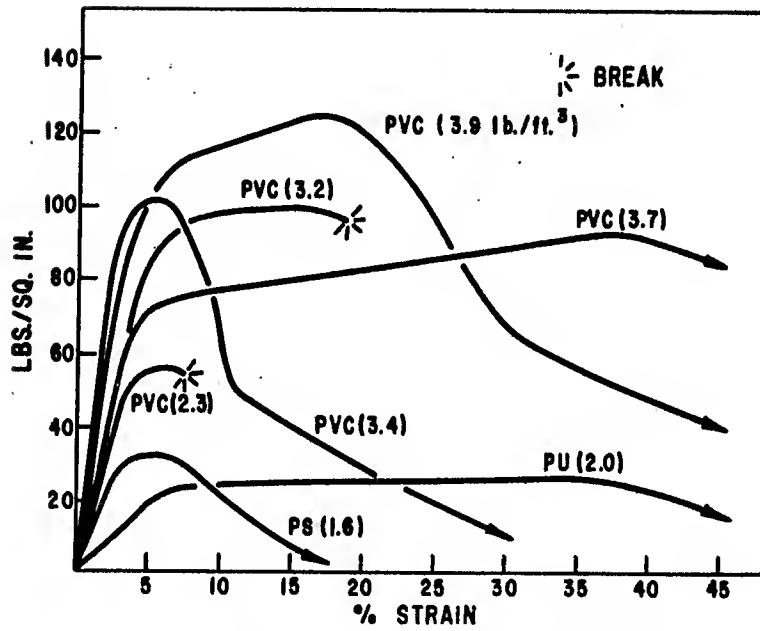


Figure 16. RIGID FOAM SHEAR CURVES

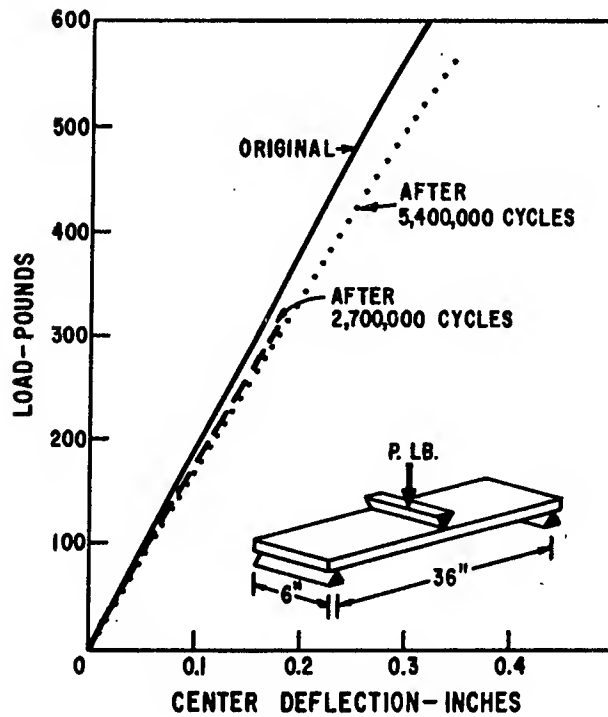


Figure 17. FATIGUE RESISTANCE

strength. The beam again was flexed for 50 hours and then tested to destruction. There was very little deterioration in strength or stiffness after 5.4 million flexes.

For another test the trailing edge of a helicopter blade was filled with foam having a density of 2.5 lbs/ft³. The blade was revolved 70,000,000 times at 1300 cycles per minute followed by 70,000,000 revolutions at 2000 cycles/min. (Actual flight conditions are 370 cycles/min.) The test did not cause any distortion or delamination of the foam.

Thermal Conductivity

Comparative insulating properties of foams having a density of 2 lbs/ft³ are shown as a function of density in Figure 18. The aged samples were heated in a dry oven at 80°C. for four weeks before testing. A 72°F. temperature drop was maintained across the test sample. Fresh polyurethane has a marked advantage above -25°F.. Aged PVC foam can be a better insulator than aged polyurethane between 30°F. and -100°F..

Porosity and Moisture Vapor Transmission

A low open-cell content and low moisture vapor permeability in a foam is important for retention of insulating value, especially at low temperatures. This is particularly important where accidental damage to surface covering may occur in service. The

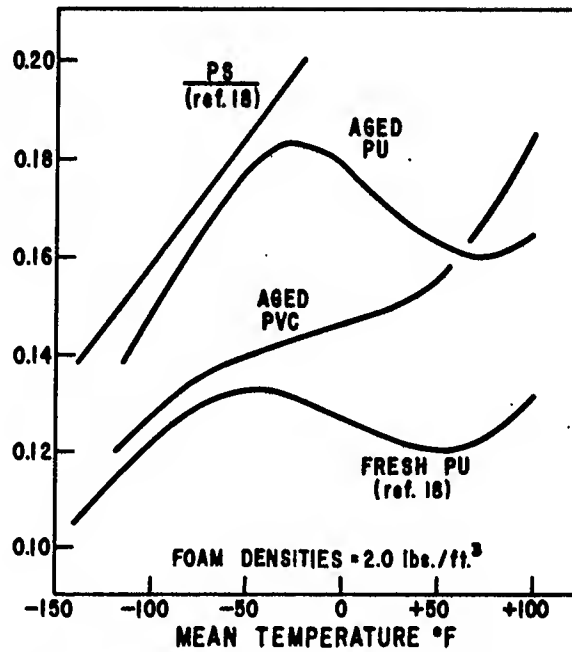


Figure 18. THERMAL CONDUCTIVITY OF FOAMS
vs. TEMPERATURE

following data on porosity was determined by the method of
Harding²² using ASTM D 1940-62T. MVT was determined
according to ASTM C-355-64.

	<u>Density(# /ft³)</u>	<u>Porosity (%)</u>	<u>MVT(perm-in.)</u>
Polyurethane	1.7	1.5	.92
Polystyrene	1.8	2.5	.92
PVC-NCO	1.7	2.8	.21
PVC-NCO	3.9	1.1	.03
Polyethylene	2.0	0.5	.04

Flammability

The PVC-NCO foams soften and distort in a fire but they do not melt or drip. They rate as non-burning by Underwriters Tunnel Test (E 84). Foam with a density of 1.5 lbs/ft³ had a rating of 15. The rating was 20 at 2.0 lbs/ft³. In common with other flame-resistant foams, considerable smoke is generated. Consequently they are more suitable for use in flameproof inhabited structures than in combustible ones.

Coefficient of Thermal Expansion

Where insulation is bonded to a facing material, the use of the sandwich at a temperature considerably lower than the bonding temperature can induce bond failure because of the difference in thermal expansion coefficients between the two materials. Strains in a panel made with PVC foam would be lower as indicated by the following coefficients.

	<u>Coefficient</u>	<u>Temp. Range</u>
Polyurethane	$4 \times 10^{-5}/^{\circ}\text{F}$	70 to -196 °C
Polystyrene	$3 \times 10^{-5}/^{\circ}\text{F}$	---
PVC G-300	$2 \times 10^{-5}/^{\circ}\text{F}$	70 to -196 °C
Aluminum	$1.3 \times 10^{-5}/^{\circ}\text{F}$	---

Applications

The greatest utility of rigid PVC-NCO foams, relative to other foams, occurs in applications where both strength and

insulating properties are important. They can be used wherever slab stock can be used. They cost about as much as flame-resistant polyurethanes.

At present about half of the output in Europe goes into refrigerated transport, mainly trucks and railcars. The foam is used as the insulating medium and as the structural core of a sandwich laminate. Commonly, complete vehicle sides are prefabricated in one bonding operation.²³ In order to use the high strength of the core foam the facing sheeting must be clean, and primed in some cases. And the lamination should be done at a pressure of 5 psi with a strong durable adhesive such as a modified epoxy. The non friability, relatively low coefficient of thermal expansion, strength, and fatigue resistance of the foam impart durability to the bonded structure. The prefabricated, frameless construction requires less construction time, saves weight and reduces heat loss compared to conventional framed structures. The foam has been used also in a number of insulated tankers built for carrying liquified methane at -160°C. from Africa to Europe.

About 15% of the foam is used in the construction industry. High structural strength, insulation and flame resistance are important requirements. Because the foam has good solvent resistance, panels can be constructed using a variety of adhesives. The panels are generally used for commercial and industrial curtain walls.

In other applications, the elastic rigidity, fire resistance and light weight of the foam are most important. About 20% of present output is used for marine and aircraft applications. Small boats, made of fiber glass laid up on sheets of contoured PVC foam, can absorb severe racking and pounding without damage. In addition they are light and nonsinkable.

Air craft deck panels with thin metal skins enclosing PVC foam with a density of 4-6 lbs/ft³ have excellent fatigue life and high strength to weight ratios. They are capable of withstanding, without core damage, relatively large local deformations caused by ladies high heels and other severe abuses such as freight-case corners. (24) A deck panel 0.4 inches thick may be constructed, for example, of 4.5 lbs/ft³ foam and skins of aluminum alloy only .012-.016 inches thick. It will not fail under the weight of two passengers in their seats until a force of 9 G is exceeded. PVC foam has also been used in pontoons, ailerons and bulkheads.

The less-expensive structural PVC foams weighing 1.5 lbs/ft³ are a fairly recent development. It is probable that further uses will be found for them soon in construction and in industrial insulation. At present PVC foams probably have less than one per cent of the rigid foam market in the United States. They

consume far less than one per cent of the PVC used for rigid products which in turn use only about ten per cent of total PVC production.

The foams I have just described are real greenhorns in this country.

And they are up against the polyurethane-polystyrene establishment.

Time will tell how well they make the scene.

REFERENCES

- (1) Barr, J. T. , Advances in Petroleum Chem. & Refining, Vol. 7, New York, (1963) Chapter 7, Polyvinyl Chloride.
- (2) Penn, W. S. , PVC Technology, MacLaren & Sons, London, (1962).
- (3) Meyer, R. J., and Esarove, D. , "High Density Cellular Vinyl by Direct Extrusion", Plastics Technology, March, (1959).
- (4) Esarove, D. , and Meyer, R. J. , "Low Density Cellular Vinyl by Post Expansion Methods", Plastics Technology.
- (5) Meyer, R. J. , "Trends in Foamed Vinyl Processing", Chem. Eng. Prog. , Vol. 57, No. 11.
- (6) Brit, P. , 892,086, (1962) (Chemische Werke Hüls).
- (7) Kalinowska, R. , and Sluzewska, L. , Roczniki Państwowego Zakładu 10, 117-31, (1959).
- (8) Baschant, E. , "Importance of PVC Foam and Its Possibilities", Kuntstoffe 44, 542-6, (1954).
- (9) US 2,737,503 (1956); US 2,901,446 (1959); Brit 853,944 (1960); Belg 624,548 (1963); US 3,122,515 (1964); Fr 1,350,696 (1964).
- (10) Chapman, F. , "Expanded PVC", Trans. Inst. Rub. Ind. 34, No. 3.
- (11) U. S. P. 3,020,248 (1962); Belg 654,348 (1965) (Dynamit Nobel).
- (12) Brit 686,310 (1953); US 2,737,503 (1956); US 2,746,940 (1956).
- (13) U. S. P. 2,965,586 (1960).
- (14) (a) Brit 686,310 (1953); (b) US 2,589,537 (1952); (c) US 2,658,043 (1953).
- (15) Chem. & Eng. News, December 12, 1966, page 42.

- (16) (a) US 2,576,749 (1951); (b) Brit 921,068 (1963); (c) Fr 1,256,549 (1961); (d) US 3,200,089 (1965); (e) US 3,256,217 (1966); (f) Brit 1,014,502 (1965); (g) Brit 993,763 (1965); (h) Fr 1,345,107 (1963); (i) Fr 1,366,979 (1964); (j) Brit 997,318 (1965).
- (17) 'Some Mechanical and Physical Properties of Klegecell' (Kléber-Colombes Report).
- (18) 'Plastic Foams', Materials in Design Engineering, Pg. 94, May, (1966).
- (19) Tariel, H. M., et al, 'Klegecell Thermal Insulation for Liquid Hydrogen Tank of Cryogenic Stage' (1966 Cryogenic Engineering Conference, June 1966, Boulder, Colorado.
- (20) Phillips, T. L., and Lannon, D. A., "The Assessment of the Physical Properties of Rigid Expanded Plastics", British Plastics, May, (1961).
- (21) King, Paddy, 'Building with Expanded PVC Panels', Automotive Design Engineering, November, (1962).
- (22) Harding, R. H., Modern Plastics, 37, p 156, 1960.
- (23) Plasticell in Vehicles Kh6 4/1, 4/2, 4/3; BTR Industries Limited.
- (24) Laminated Metal Sandwich Structures for Aircraft; Palmer Aero Products Limited.

10214-11

STYRENE BUTADIENE FOAMS

^{B.L.}
R. L. Zimmerman
The Dow Chemical Company
Midland, Michigan

STYRENE BUTADIENE FOAMS

The use of styrene-butadiene copolymers in cellular products began as a result of the availability of latex and gum stock from World War II synthetic rubber programs. GR-S was the early designation and later SBR was used to identify these materials. Applications primarily developed in the field of flexible cushion products based on high butadiene elastomers with only a minor role for high styrene copolymers in alloys or blends. One summary of market data is given in Table I, which estimates latex and sponge consumption in the United States by product and also by type of rubber.

TABLE I. MARKET FOR FOAMS

A. Sponge Versus Latex

	Estimated Consumption (MM Lbs.)				
	1962	1963	1964	1965	1970
Sponge	<u>82</u>	<u>82</u>	<u>81</u>	<u>80</u>	<u>75</u>
Latex	140	135	130	125	110

B. Breakdown by Rubber Type

	Estimated Consumption (MM Lbs.)				
	1962	1963	1964	1965	1970
SBR	<u>80</u>	<u>95</u>	<u>100</u>	<u>105</u>	<u>120</u>
Natural	49	52	56	60	75
Polyisoprene	8	12	17	20	34
Neoprene	0.5	1	1	2	4

Source: "United States Foamed Plastics Market and Directory - 1964", Technomic Publishing Company, - Stamford, Conn.

In the United States, SBR constitutes the major component of cellular elastomer products, ^{Natural rubber} and held 15% of the United States foam latex market in 1964, down from 50% in 1959. By comparison, in the United Kingdom, natural latex constituted 60% of the foam latex consumed in 1964 and 100% of the 1959 market.

After World War II SBR latex found its way into the already developed Dunlop and Talalay processes for production of latex foam as partial replacement for natural latex while gum stocks were introduced into recipes for molded and extruded products where a blowing agent was used to generate the cell structure. The terms "latex foam" and "blown sponge" describe two distinct classes which should be clearly differentiated. Latex foam can only be made in open cell form whereas blown sponge can be made open cell or closed cell, or both, depending on the mode of manufacture.

The relationship between foam and sponge may be clarified by considering the origin and handling of the styrene-butadiene copolymer used in each case. Rubber for sponge is basically the same as rubber used in tire production. The majority of this SBR is synthesized by continuous emulsion polymerization at low solids with short stopping, monomer stripping and coagulation to crumb followed by conversion to crepe and bale form. Sponge recipes are compounded on a two roll mill, or in a closed mixer, followed by a pre-cure in some cases and then fabrication by molding, extrusion or calendaring. Sulfur vulcanization cure is accomplished by time and temperature cycles related to bulk rubber production but taking into account generally lower heat transfer rates. The crucial aspect of the operation is the decomposition of a gas-releasing blowing agent which must be timed to accomplish the desired blowing and cell structuring when the compound has the proper rheology.

Latexes for foam are also synthesized by emulsion polymerization using both continuous and batch methods. Monomer stripping is generally followed by agglomeration to larger particle size and concentration to high solids (58 - 72%). Compounding of ingredients for a vulcanization recipe is done on a wet basis, often with two or three separate mixes to keep reactive ingredients from acting too early. The latex compound may require maturing to achieve some desired level of polymer conditioning before foaming. The latter consists simply of continuous or batch mixing of the final latex compound with air in a foaming machine. In the Dunlop process, a gelling agent is added so that in a time of the order of 5 - 10 minutes after foaming the froth will set to a structurally firm gel. The froth is poured in molds or coated before gelation and then heated to first gel and finally dry the foam. Water can be squeezed from a structurally strong gel before drying to hasten drying and curing.

In the Talalay process, the froth (without gelling agent) is put in a mold and a vacuum applied followed by freezing and treatment with carbon dioxide to gel the foam which is subsequently vulcanized and dried.

A more extensive discussion of sponge rubber technology, taken from the literature, will be given including an example detailing the manufacture of carpet underlay. The remainder of the paper will be devoted to latex foam covering vulcanized foam and then the new area of chemically cured foam based on carboxylated styrene butadiene latex, which is the author's field of specialization.

BLOWN SPONGE

As indicated above, the critical aspect of SBR sponge production is properly timing the generation of the gas in the heated rubber.

Figure 1 is helpful in understanding the changes in viscosity when a thermoplastic uncured rubber mixture is heated and then cross-linked by vulcanization. A too low initial viscosity or too early release of gas from the blowing agent while the viscosity is decreasing (Area A) results in the gas bubbles going through the mass and either escaping or combining to form a useless end product. Release of gas near the low point of viscosity (Area B) tends to trap the bubbles in a cell of rubber film, and the whole mass expands like baking bread. Because the film membranes are weak in this case they normally break, and result in open-cell sponge. Decomposition of the blowing agent at high viscosity (Area C) produces closed cells because the cell walls are strong enough to prevent rupture. Lack of expansion or very dense products results if gas release occurs still later in the vulcanization process.

Starting with highly viscous or nonthermoplastic rubber, such as high-molecular weight SBR, it is difficult to obtain good sponge processing. Therefore, plasticizers, masticated rubber or low-molecular weight (low-Mooney viscosity) polymer are preferred which in the extreme can yield substantially a liquid or dough-like mass before curing begins, which is desirable for open-cell products. Carbon dioxide from reaction of sodium or ammonium bicarbonate with stearic acid, oleic acid, or alum is often employed as the blowing agent.

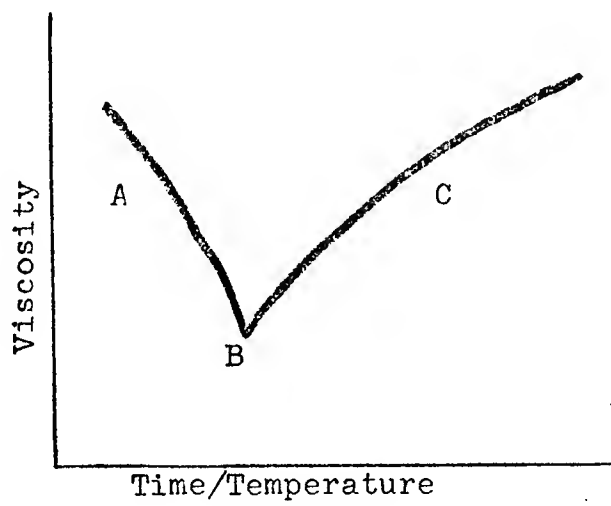


Fig. 1 -- Time-temperature effects on viscosity

For most closed-cell sponge higher Mooney viscosity rubber is employed and nitrogen must be used for blowing to prevent collapse during and after cooling when the internal cell pressure is undergoing equalization by permeation. Expansion occurs in three dimensions (compared with unidirectional expansion of open-cell sponge) creating severe heat transfer problems in a mold. A precure heating and expansion cycle is performed using a confining mold. After removal from the mold, the part will expand and may be heated in an oven before final expansion and cure in an exact-size mold. A molding method based on partially expanded pellets enclosed in a calendared skin can also be used.

Extrusion of partially closed cell sponge is based on high viscosity rubber, fast cure and use of a high-temperature nitrogen releasing blowing agent. Extrusion and calendaring can also be used for closed cell sponge in a free expansion process. The shaped compound is simply heated in an oven to temperatures above the decomposition point of the blowing agent with careful control to assure a precise balance between vulcanization and expansion. The oldest method for closed cell sponge starts with partial vulcanization of the rubber, pressurization with nitrogen in a press at 3,000 to 5,000 p.s.i. to dissolve gas in the rubber, expansion and final cure in a mold.

Carpet underlay manufacture generally involves a combination of nitrogen and carbon dioxide producing blowing agents to give a

combination of open and closed-cells. A typical formulation is detailed in Table II. Compounding of these ingredients forms a paste-like mix that is usually sheeted on a three or four roll calendar and doubled onto a scrim backing, which rides on a belt through a 50 to 200 foot oven. Cure takes about five minutes at 320-340°F, and the sponge expands about 100%. A chain belt laid on the green sheet produces a waffle-like pattern after expansion. This type of sponge underlay is manufactured in 54 inch, 6 feet, and 9 feet widths in a variety of thicknesses. It has achieved excellent market acceptance showing a growth rate of 40% per year from 1963 to 1965. In 1965 the market for sponge underlay was about 117 million square yards.

TABLE II. SPONGE UNDERLAY FORMULATION

	<u>Parts by Weight</u>
SBR and/or Natural Rubber	100
Zinc Oxide	5
Clay or Whiting	100-270
Process Oil	20-50
Petrolatum	3
Paraffin Wax	1
Sodium Bicarbonate	8-12
Stearic Acid	6-8
"Celogen" Blowing Agent	0.5
"MBTS" Accelerator	2
"Cyuran" MS Accelerator	0.5
Antioxidant	1
Sulfur	3

VULCANIZED FOAM LATEX

The essential features of latex foam manufacture are (1) aeration of a latex compound, (2) stabilization of the froth, (3) removal of water and (4) cross-linking the rubber. Foam latex consists of copolymer particles up to about 10,000 Å size dispersed in water with a surface active agent or soap that prevents the particles from coalescing. Large particle size and broad size distribution are needed for attaining the desired high solids. After frothing with air, the dispersant can be rendered ineffective by adding a gelling agent which causes a drop in pH and destabilizes the surfactant as by conversion of a soap to its fatty acid. Freezing provides another means for initialing coalescence. The particles can also be coalesced by drying, dehydration (as by addition of alcohol), bacterial action that acidifies the medium, and prolonged heating. Union of the latex particles generates a film or polymeric binder structure around the air bubbles and stabilizes the foam. Mechanical stress induced by freezing, water evaporation and squeezing breaks the cell wall film resulting in an interconnecting open cell structure. Additional microporosity may also be produced by escape of water trapped by vulcanization in a wet gel.

The Dunlop process (9) for latex foam production is based on salts of hydrofluorosilic acid (specifically Na_2SiF_6 and K_2SiF_6) to gel or solidify the wet froth. In this process, timing of gelation and soap decomposition is very important to foam structure. A gel time of five minutes, and a soap time of seven minutes, are considered normal and result in foam shrinkage of roughly 20%. A

greater time spread than this tends to produce a stringy condition resulting in low compression resistance and poor strength due to disconnected columns in the foam structure. If gel time and soap time are too fast, additional foam collapse may occur resulting in excessive shrinking. In the extreme, if the soap decomposes before gelation, the whole mass collapses. Thus, compounding and foam processing require careful control of ingredients and methods for reproducible foam production. In some respects there is more art than science involved in dealing with the problems that can arise.

In the modern Talalay process, (10) foam is formed in a mold by application of a vacuum to an aerated compound, the froth is then frozen which causes the foam cells to interconnect and carbon dioxide gas is introduced breaking the vacuum and resulting in gelation as the foam is brought back to room temperature. The mold is then heated to about 230°F to vulcanize the foam, after which it can be stripped from the mold, washed and dried. A complete cycle lasts from 30 to 40 minutes. A uniform cell size and improved cell structure are obtained compared with the Dunlop process. This results in better load carrying properties. Pin-core foam blocks represent an improvement in the form of this type foam particularly for the furniture and bedding markets.

One of the major uses for latex foam is in textile coatings. Carpet backing, carpet underlay, washable padded undergarments, shoe insoles and automotive linings are the main applications. In general,

the Dunlop process is used for vulcanized foam coating of textiles although numerous modifications are practiced. Typical recipes are given in Table III, which shows the breakdown of ingredients into Parts A, B, and C. For prolonged storage, the Trimene Base rubber accelerator and sulfur of Part A should be put in Part B. The percent solids shown may need to be lowered for low density foam because the froth viscosity is inversely proportional to the froth density. Parts A and B are mixed when the compound is to be used and are pumped to a continuous foam machine such as the Oakes Continuous Mixer. Part C, the gelling agent, is introduced as a separate stream at the mixer. The theory of zinc ammonium salt gelling of latex is discussed in detail by Madge (2). Complexed zinc amine ions are believed to be responsible for gelation together with the formation of insoluble zinc soap. Gelation is dependent on concentration of several ingredients and the pH. At high pH unreactive tetramine predominates, and if there is no excess of ammonium salt, zinc soaps are not formed. Heating dissociates the tetramine complexes resulting in zinc soap formation and consequent gelation. Addition of ammonium acetate as a gelling agent is done at carefully adjusted compound pH and gellant pH in order to provide processing latitude between the limiting amounts of ammonium salt and permit proper timing of gelation.

The frothed latex compound is spread on the textile backing, for example, the back of a carpet, and doctored to a uniform coating with a roll or knife across the width of the goods. Surface or

TABLE III. SPREAD FOAM COMPOUNDS

Typical Total Solids Part "A"		Parts by Weight Dry		
		A	B	C
66	"POLYSAR" Latex 725	100.0	100.0	100.0
60	Sodium Lauryl Sulphonate	0.25	0.25	0.25
20	Potassium Salt of Tall Oil	1.50	2.50	3.50
50	Trimene Base"	1.00	1.00	1.00
50	Zinc Diethyldithiocarbamate	1.50	1.50	1.50
50	Zinc Mercaptobenzo-thiazole	1.00	1.00	1.00
60	Sulphur	2.00	2.00	2.00
50	Antioxidant	1.00	1.00	1.00
28	Ammonia	0.75	0.75	0.75
100	Filler	100.0	150.0	200.0
Water to Compound Solids of		73%	74%	75%
10	Potassium Hydroxide	←To Compound pH of 11.7→		
Part "B"				
20	Potassium Salt of Tall Oil	0.5	0.5	0.5
50	Zinc Oxide	3.0	3.0	3.0
Part "C"				
20	Ammonium Acetate (pH 9.7)	2.50	2.50	2.50

pre-gelling may be effected with infrared lamps or radio frequency heaters followed by drying and vulcanization in an oven at temperatures above 300°F.

CARBOXYLATED STYRENE BUTADIENE FOAM

One of the newest developments in latex foam is an invention of The Dow Chemical Company for production of foam based on chemically reactive latexes cured with a co-reactive agent rather than by vulcanization. Applications have been made for United States and foreign patents (5), and a licensing program has been formulated. The Dow Latex Foam Process teaches operability of a wide variety of polymer types, and a number of reactive functional groups, but field development has centered on styrene-butadiene latex with carboxylic functionality.

Carboxylated latexes exhibit excellent mechanical and chemical stability. The acid groups contribute tenacity, adhesion and abrasion resistance to the polymer. Amine-formaldehyde resins and especially melamine-formaldehyde with or without methylation have been found well suited for curing the latex polymer.

Table IV is a basic recipe illustrating the ingredients used for making foam by the Dow process. A two-part formulation is used for maintaining shelf stability. Variation in Cyrez reactive resin type and amount is shown and results in the property differences tabulated in Table V. A destabilizing agent such as sodium silicofluoride can be employed for room temperature gelation, but in heat processed foams this additive is of no real advantage.

For laboratory test specimens the compounded formulation is whipped as a batch in a planetary mixer and doctored onto a fiber glass screen coated with Teflon plastic, which permits moisture to escape through it and from which the dried foam will readily release. The wet foam is exposed to infrared heat briefly to toughen the surface against the blast of air in a forced air circulating oven. A thermocouple placed in the center of the foam is used to measure the center line temperature. The foam is removed when the center temperature reaches about 310°F.

TABLE IV. LATEX FOAM COMPOUNDS

Part "A"		Total	Dry Parts
		<u>Solids, %</u>	<u>By Weight</u>
Basic Recipe			
Dow Latex 902		58	100.0
Frothing Agent		30	2.0
Lubricant		100	1.0
Filler		100	100.0
Froth Stabilizer		2.5	0.25
Part "B"			
Compound			Dry Parts
<u>Number</u>			<u>By Weight</u>
1	Cyrez 711		5.0
2	Cyrez 711		7.5
3	Cyrez 711		10.0
4	Cyrez 933		5.0
5	Cyrez 933		7.5
6	Cyrez 933		10.0
7	Cyrez 711 - Cyrez 933		7.5

Drying of the foam, of course, occurs from the outer surfaces toward the center and the dried foam becomes a good heat insulator, therefore, there is a practical limit of about one-half inch to the thickness of foam that can be prepared without getting a significant difference of the outer shell, and the central portion of the foam. Squeezing water from the foam is usually not feasible because the formulation does not produce a mechanically strong foam until the water has been evaporated. Low wet gel strength also prevents closed die molding from being practical. Measurements of foam dimensions on drying indicate that little or no shrinkage is associated with the drying process.

The striking feature of carboxylated latex foam processing versus vulcanized foam technology is the relative simplicity of the system. There is also a basic difference in that for the system described, particle coalescence occurs by drying rather than by the gelation mechanism or by the freezing and carbon dioxide treatment as in the Dunlop or Talalay processes. The froth is simply stabilized during drying so that little or no cell degradation is involved and thus a very fine cell structure is formed.

Finished foams have been tested (See appendix for test methods) and the data are displayed in Tables V and VI. Besides variation in reactive resin type and amount, latex pH, foam density, cure time, and filler type have been investigated using Compound Number 7 (Table IV)

The reactive melamine-formaldehyde resins offer considerable versatility in foam processing and in foam properties (Table V). A mixture of resins has been preferred for optimizing some advantages of each. Wet froth stability relates to latex pH with a maximum in gauge retention (final thickness versus cast thickness) occurring at a pH of 9.5. Resultant foams exhibited a maximum in compression load deflection (CLD) at the same pH.

TABLE V. FINISHED FOAM PROPERTIES

	CURE TEMPERATURE 325°F						
			Compound Number				
	1	2	3	4	5	6	7
Cure Time, min.	19	22	21	21	21	22	20
Density, lb./cu. ft.	9.6	11.1	10.4	10.0	10.4	10.8	10.3
Gain in Gauge, %	5.6	11.8	7.5	12.8	10.4	10.4	9.9
Comp. Resist., CLD lb/50 sq. in.	52	94	90	83	115	139	103
Tensile, lb./in. ²	13.8	17.4	17.9	20.5	24.6	27.9	23.1
Elongation, %	180	160	155	210	140	120	150
Compression Set, %	12	9.4	8.7	11.5	12.3	16.0	11.5
Resilience, %	15	16.5	15	15	14.5	14.5	14.5

Foam density, of course, is a direct function of the amount of air that is whipped into the latex compound. Foams in the range of 5 to 15 pound/foot³ and higher are readily prepared with resultant gauge retention varying from -3 to +40%. Firmness increases from roughly 20 to 200 pound/50 inch², tensile strength from about 7

to 30 pound/inch² over the same range, elongation falls off from 190 to 150% and compression set from 18 to 9% for foams based on Compound Number 7.

Oven dwell or cure time is quite critical for the development of good properties. Severe undercure and overcure result in weak foam whereas compression set resistance requires more time to develop but does not deteriorate with moderately extended cure.

As illustrated in Table VI, the type of filler loading has a significant effect on foam properties. Increased loading results mainly in tensile/elongation deterioration.

In Figure 2 the compression hysteresis loop for one cycle shows a loss of recovery force on removal of the load for a foam of 11.2 pound/foot³ density. Continued cycling results in early dynamic flex fatigue within about 1000 cycles of flexing to 50 per cent gauge in the Raygus flex test and is followed by almost no additional loss up to 250,000 cycles. Thickness loss after dynamic flexing is less than two per cent.

Foams made by the Dow process exhibit several novel characteristics including uniform fine cell structure, a velvety hand, whiteness and absence of copper staining. Favorable properties also include low odor, good abrasion resistance, high load bearing, heat resistance, light resistance and gas fade resistance. Solvent

TABLE VI

FILLER STUDY

All Foams Cast At 0.375"

Amount	Brand or Type	Density lb./ft ³	Thickness	25% CLD-9 @ 10#/ft ³	Compression Set	Tensile @10#/ft ³	Elongation (%)
100	Atomite	11.7	0.366"	68#/50in ²	12.1%	22.0 psi	145
100	Snowflake White	10.8	0.385"	76	10.4%	21.9	159
100	Duramite	10.4	0.376"	81	12.1%	21.4	178
100	Drikalite	10.2	0.382"	84	9.6%	22.5	153
100	#9 Whiting	10.9	0.376"	60	11.0%	18.7	195
100	#10 Whiting	9.3	0.379"	95	10.1%	22.5	168
100	York Whiting	10.5	0.372"	73	10.8%	20.3	176
100	Alumina Hydrate	10.4	0.392"	54	11.9%	19.5	176
100	Lufil	10.1	0.387"	81	17.2%	19.2	231
100	Lufil 400	9.4	0.386"	91	10.9%	21.9	206
100	CWF Clay	10.7	0.378"	113	10.6%	22.2	116
2.5	Bentonite 200						
97.5	Alumina Hydrate	9.7	0.385"	57	11.0%	18.2	223
10	Philblack A						
90	Alumina Hydrate	12.3	0.384"	44	10.6%	15.5	170
100	Silvery Talc	9.7	0.402"	96	14.6%	20.9	178
100	Super 325 Talc						
100	Mistron Frost						
	Talc						
100	WG Mica 325	10.2	0.388"	62	11.4%	20.8	163
100	Kaoloid Clay	9.6	0.400"	103	27.0%	16.0	90-95
10	ASP 100						
90	Alumina Hydrate	10.1	0.389"	66	16.3%	20.2	186
10	ASP 400						
90	Alumina Hydrate	9.9	0.374"	63	15.6%	19.3	188

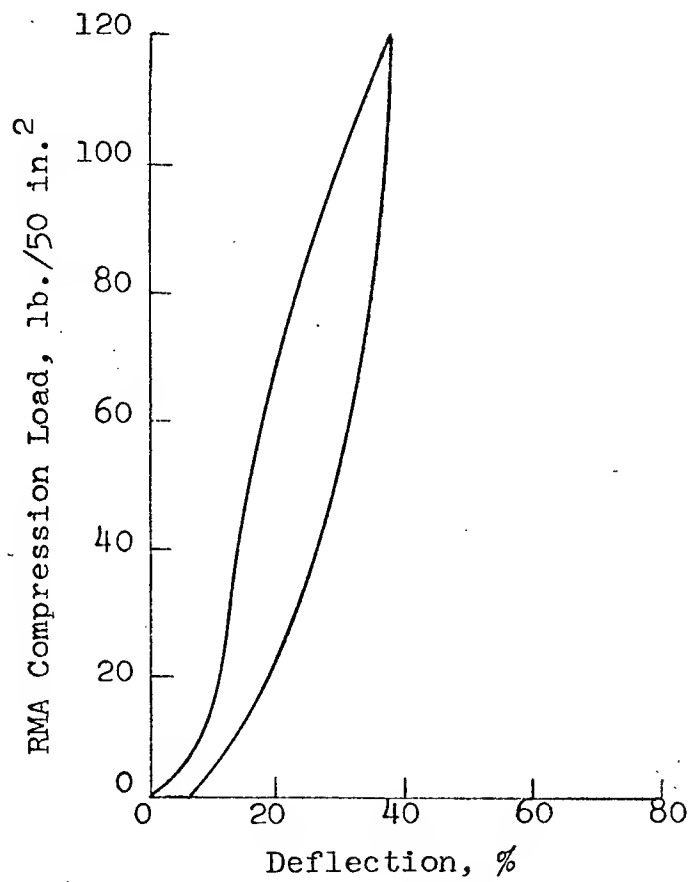


Fig. 2 -- Compression Hysteresis

resistance is fairly good, but the strength of saturated foam is not adequate to permit dry cleaning.

Because of the excellent adhesion of carboxylated styrene/butadiene latex to a wide variety of materials the foam products are uniquely suited for coatings. The substrate, naturally, plays a significant part in the processing and final character of the finished article. Cellulosics, wool, natural fibers, mineral fibers and some films capable of withstanding temperatures of about 300°F for five to ten minutes can be successfully coated. Treated substrates may release volatile materials that could cause foam collapse or striation so that evaluation is required to determine compatibility with the system.

Minimum strike through of the doctored froth is a significant advantage that can be realized and sufficient mechanical strength is obtained to permit laying a top fabric on the wet foam. It is essential, however, that at least one surface and preferably both surfaces permit passage of water vapor during drying.

Commercial foam has been produced since 1963 by firms licensed to make latex foam by the Dow process. Foam on carpet and rugs as well as carpet underlay are suitable applications. Fabric coated foam for washable undergarments, bathing suits and canvas shoe uppers are additional areas where introduction of the foam has been significant. Newer uses include foam for shoe insoles, automotive lining and cushion coatings.

BIBLIOGRAPHY

- (1) Zimmerman, R. L., Hibbard, B. B. and Bailey, H. R.,
Rubber Age 98, 5, 68 (1966)
- (2) Madge, E. W., Latex Foam Rubber, London Maclaren (1962)
- (3) Rogers, T. H., SPE Journal 22, 49 (1966)
- (4) Angove S. N., Rubber and Plastics Age 47, 10, 1090 (1966)
- (5) Dunn, E. R., United States Patent 3,215,647 (November 2, 1965)
- (6) Calvert, K. O. and Newnham, J. L. M., -- Rubber Age 98, 2, 73
(1966)
- (7) Angove, S. N. ACS Rubber Division Meeting, New York, September,
(1966)
- (8) Bascom, R. C., Rubber Age 96, 7, 576 (1964)
- (9) Chapman, Pounds and Murphy, United States Patent 1,852,447
(April 5, 1932)
- (10) Tallalay, J., United States Patent 2,140,062 (December 13, 1938)

APPENDIX

Test Methods

- (1) Conditioning -- Foams were aged 24 ± 4 hours at $73.4 \pm 2^{\circ}\text{F}$
and $50 \pm 2\%$ relative humidity prior to testing.
- (2) Compression Resistance -- (A) CLD -- Compression load deflec-
tion was measured with an Aminco-Frazier compressometer having
a one inch diameter foot. Test specimens were cut with a
1.129 inch diameter die, preflexed three times to 50 per cent
deflection and the load measured at 25 per cent deflection.
The average value of four samples was determined and reported

as the load for 50 square inches. (B) RMA -- A link compression tester was used for the standard Rubber Manufacturers Association compression load test.

- (3) Resilience -- The test used was ASTM D1564-63T, Suffix R, Section 88-94 modified in that samples 3/8 inch thick instead of two inches were employed. Two plys of foam were required if the foam bottomed out.
- (4) Compression Set -- Samples 2" x 2" compressed 50% for 22 hours at 158°F were measured 30 minutes after release and the set reported as per cent of original height.
- (5) Tensile Strength and Elongation -- Die cut dumbbell shaped specimens were pulled at 20 in./min. on an Instron Tester. Tensile strength and elongation of two marks initially one inch apart were determined at rupture and averaged for four specimens.

10214-12

THE PRODUCTION AND THERMOFORMING OF POLYSTYRENE FOAM SHEET

BY
TED P. MARTENS
SINCLAIR-KOPPERS COMPANY
PRODUCT DEVELOPMENT DEPARTMENT
MONACA, PENNSYLVANIA

TO BE PRESENTED AT THE 1967
POLYMER CONFERENCE SERIES
WAYNE STATE UNIVERSITY
DETROIT, MICHIGAN

THE PRODUCTION AND THERMOFORMING OF POLYSTYRENE FOAM SHEET

10214-12

EXPANDABLE POLYSTYRENE IS PROBABLY BEST KNOWN IN THE BEAD MOLDED FORM WHERE SUCH ITEMS AS PICNIC COOLERS, HOT DRINK CUPS, AND NUMEROUS PACKAGING ITEMS ARE ENCOUNTERED DAILY. IT CAN ALSO BE PRODUCED IN THE FORM OF EXTRUDED FILM OR SHEET WHICH CAN BE SUBSEQUENTLY THERMOFORMED INTO A VARIETY OF END-USE PRODUCTS. WITH THE RAPID GROWTH OF APPLICATIONS FOR THESE THERMOFORMED PRODUCTS IN THE PAST FEW YEARS, THE EXTRUSION PROCESS HAS BECOME AN IMPORTANT PROCESSING TECHNIQUE.

EXTRUSION SYSTEMS

THREE SYSTEMS ARE IN USE TO PRODUCE FOAM POLYSTYRENE SHEET. THE ORIGINAL WAS A SINGLE STEP EXTRUSION PROCESS WHERE THE RAW MATERIAL WAS A FOAMABLE PELLET CONTAINING A HYDROCARBON BLOWING AGENT. THE OTHER TWO SYSTEMS ARE USUALLY REFERRED TO AS DIRECT INJECTION SYSTEMS. ONE INJECTION SYSTEM USES CRYSTAL POLYSTYRENE AS A RAW MATERIAL AND BY INJECTING A HYDROCARBON BLOWING AGENT THROUGH THE EXTRUDER BARREL, FOAMABLE PELLETS ARE PRODUCED. THESE PELLETS ARE THEN EXTRUDED IN A SECOND STEP TO PRODUCE FOAM SHEET. IN SOME CASES THE FOAMABLE PELLETS ARE PRODUCED BY A STEEPING OR SOAKING PROCESS RATHER THAN BY INJECTION. THE THIRD SYSTEM COMBINES THE TWO STEPS OF THE PREVIOUS METHOD INTO A SINGLE OPERATION, WHERE THE RAW MATERIAL IS CRYSTAL POLYSTYRENE AND THE END-PRODUCT THROUGH INJECTION OF A HYDROCARBON BLOWING AGENT, IS FOAM SHEET. THIS MAY BE ACCOMPLISHED IN EITHER A SINGLE EXTRUDER OR WITH TWO EXTRUDERS DIRECTLY COUPLED TOGETHER. THE DISCUSSION HERE IS LIMITED TO THE FIRST SYSTEM FOR PRODUCING FOAM SHEET: EXTRUSION FROM A FOAMABLE BEAD OR PELLET. THE DIFFERENCES BETWEEN THE EXTRUSION SYSTEMS, HOWEVER, LIE PRIMARILY IN THE EXTRUDER ITSELF, AND THE PRINCIPLES THAT APPLY FOR DIE DESIGN, TAKE AWAY, AND WINDING GENERALLY HOLD TRUE FOR ALL SYSTEMS.

SHEET CLASSIFICATIONS

THREE TYPES OF FOAM SHEET HAVE BEEN PRODUCED FROM FOAMABLE RAW MATERIALS, AND THESE TYPES CLASSIFIED BY DENSITY. LOW DENSITY GENERALLY IMPLIES A FOAM SHEET HAVING AN ACTUAL DENSITY OF FROM 4 TO 10 POUNDS PER CUBIC FOOT, AND WITHIN THIS CATEGORY THE MOST COMMON DENSITY RANGE IS 6 TO 8 POUNDS PER CUBIC FOOT. THE SECOND CLASSIFICATION IS THAT OF MEDIUM DENSITY EXPANDED POLYSTYRENE SHEET. THIS IMPLIES A DENSITY OF FROM 10 TO 30 POUNDS PER CUBIC FOOT, WITH THE 15 TO 20 POUND RANGE BEING THE MOST COMMON. THE THIRD CLASSIFICATION, HIGH DENSITY EXPANDED POLYSTYRENE SHEET, DENOTES ALL FOAM SHEET WITH A DENSITY ABOVE 30 POUNDS PER CUBIC FOOT. OF THESE THREE, THE MAJORITY OF INTEREST AND ACTIVITY IS CENTERED AROUND THE LOW DENSITY RANGE. LOW DENSITY SHEET IS AVAILABLE COMMERCIALY FROM A NUMBER OF SUPPLIERS AND IS PRODUCED EVEN MORE EXTENSIVELY FOR CAPTIVE USE. MEDIUM DENSITY SHEET IS NORMALLY ASSOCIATED WITH A THERMOFORMED HOT DRINK CUP, PARTICULARLY A VENDING CUP, AND IS NOT GENERALLY AVAILABLE FOR SALE TO ANY EXTENT IN SHEET FORM. THE SHEET THAT IS PRODUCED IN THIS DENSITY RANGE IS ALMOST ALL FOR CAPTIVE OPERATIONS. THE THIRD CLASSIFICATION OF HIGH DENSITY FOAM SHEET ORIGINATED SEVERAL YEARS AGO AND AT ONE TIME WAS THOUGHT TO BE THE MOST DESIRABLE DENSITY FOR THE THERMOFORMED CUP. IT HAS SINCE BEEN FOUND UNECONOMICAL, HOWEVER; AND TODAY VERY LITTLE, IF ANY, ACTIVITY EXISTS IN THIS DENSITY RANGE. THE DISCUSSION HERE WILL BE LIMITED ONLY TO LOW DENSITY FOAM SHEET, AND EVEN MORE SPECIFICALLY, 6 POUND DENSITY SHEET. A DIFFERENT EXTRUSION PROCESS, FROM THE EXTRUDER ITSELF THROUGH THE WINDER, IS REQUIRED TO PRODUCE SHEET IN THE MEDIUM AND HIGH DENSITY RANGES.

PROCESSING TECHNIQUES

THERE ARE TWO TECHNIQUES IN USE FOR THE EXTRUSION OF LOW DENSITY EXPANDED POLYSTYRENE SHEET FROM A FOAMABLE BEAD OR PELLET. THESE ARE SHOWN SCHEMATICALLY IN FIGURE 1. FOR FILM OR SHEET THICKNESSES OF LESS THAN 20 MILS,

THE ENTRAPPED AIR METHOD, SIMILAR TO THAT EMPLOYED FOR POLYETHYLENE BLOWN FILM EXTRUSION, IS NORMALLY USED. THIS TECHNIQUE CONSISTS OF BLOWING A TUBE FROM A ROUND OR ANNULAR DIE, COLLAPSING THE BUBBLE, AND THEN TRIMMING OR SLITTING THE EDGES TO OBTAIN TWO FLAT SHEETS. SINCE THE MAJORITY OF SHEET PRODUCED IS GREATER THAN 20 MILS THICK, THE SIZING PLUG TECHNIQUE IS MORE COMMON. IN THIS METHOD, THE SHEET IS PULLED OVER A SIZING MANDREL, SLIT USUALLY IN TWO PLACES, AND THEN EACH OF THE TWO SHEETS PULLED OFF INDIVIDUALLY BY A SET OF DRIVEN PULL ROLLS. FIGURES 2 AND 3 SHOW SHEET BEING PRODUCED BY THE SIZING PLUG METHOD.

RAW MATERIALS

MATERIAL TO PRODUCE FOAM SHEET IS AVAILABLE IN EITHER BEAD OR PELLET FORM. THE PELLET PRODUCT IS, BY FAR, THE MOST COMMON AND REQUIRES NO SPECIAL EXTRUSION EQUIPMENT. RECENTLY, BECAUSE OF A COST SAVINGS, INTEREST HAS ALSO BEEN EXPRESSED IN A BEAD FEED. BEADS, HOWEVER, OFTEN REQUIRE THE USE OF A FORCE FEEDING DEVICE OR COMPACTOR TO INSURE UNIFORM AND CONSISTENT DELIVERY TO THE EXTRUDER SCREW. WITH BOTH PRODUCTS, THE HYDROCARBON BLOWING AGENT, NORMALLY PENTANE, IS ALREADY ENCAPSULATED IN THE MATERIAL. IN ADDITION TO THE BLOWING AGENT, A NUCLEATING SYSTEM IS ALSO REQUIRED TO PRODUCE A SMALL CELL STRUCTURE IN THE EXTRUDED SHEET. AN EFFECTIVE SYSTEM CONSISTS OF CITRIC ACID OR SODIUM BICARBONATE.⁽¹⁾ PELLET PRODUCTS CAN BE PURCHASED WITH BOTH OF THESE NUCLEATING AGENTS ALREADY BLENDED WITH THE PRODUCT OR WITH JUST THE CITRIC ACID PORTION ENCAPSULATED. BEAD PRODUCTS, ON THE OTHER HAND, MUST BE DRY BLENDED PRIOR TO EXTRUSION WITH BOTH ADDITIVES.

EXTRUSION EQUIPMENT

IN THE EARLY DAYS OF DEVELOPMENT, IT WAS THOUGHT A BASIC POLYETHYLENE

(1) U. S. PATENTS 2,941,964, 2,941,965, AND 3,089,857 ASSIGNED TO KOPPERS CO., INC.

TYPE FILM LINE WOULD BE ADEQUATE TO PRODUCE FOAM POLYSTYRENE SHEET OF ACCEPTABLE QUALITY. BUT QUALITY STANDARDS HAVE BECOME TIGHTER AND TIGHTER, AND WITHIN THE LAST FEW YEARS IT HAS BECOME APPARENT THAT A MUCH MORE ELABORATE SYSTEM IS REQUIRED TO CONSISTENTLY PRODUCE SHEET SUITABLE FOR THERMOFORMING AND OTHER POST-EXTRUSION OPERATIONS. EXTRUDERS FOR FOAM RANGE IN SIZE FROM 2-1/2 TO 6-INCHES IN DIAMETER WITH 4-1/2-INCHES BEING THE MOST COMMON. THESE HAVE A MINIMUM L/D RATIO OF 20:1 WITH 24 OR 28:1 PROVIDING EVEN BETTER CONTROL. THE EXTRUDER BARREL SHOULD BE ELECTRICALLY HEATED AND WATER COOLED IN AT LEAST FIVE ZONES ON A 24:1, AND THE MINIMUM TEMPERATURE CONTROL PROVIDED SHOULD BE THROUGH PROPORTIONING TYPE INSTRUMENTS. SINCE VERY SMALL TEMPERATURE CHANGES SERIOUSLY AFFECT GAGE UNIFORMITY, STEP-LESS TYPE INSTRUMENTS ON THE DIE PROVIDE EVEN BETTER CONTROL. THE EXTRUDER BARREL SHOULD ALSO BE EQUIPPED WITH AT LEAST 4 POINTS FOR PRESSURE MEASUREMENT. THESE ARE NOT NORMALLY INCLUDED IN A STANDARD EXTRUDER, BUT WITH FOAM, PRESSURE INDICATION PROVIDES AN IMPORTANT DAY-TO-DAY GUIDE TO EXTRUSION UNIFORMITY AND CONSISTENCY. WHEN IT IS ANTICIPATED THAT A BEAD FEED WILL BE USED, THE EXTRUDER SHOULD ALSO BE EQUIPPED WITH SOME TYPE OF AUXILIARY FEEDING DEVICE. IF A FORCE FEEDER IS USED, IT SHOULD HAVE BOTH TORQUE AND SPEED CONTROL FOR MAXIMUM FLEXIBILITY.

THE DIE FOR FOAM POLYSTYRENE IS PROBABLY THE ONE PIECE OF EQUIPMENT THAT STILL REQUIRES THE MOST DEVELOPMENT WORK. WE KNOW OF NO DIE ON THE MARKET THAT IS ENTIRELY SATISFACTORY. FIGURES 4 AND 5 SHOW TWO DIES CURRENTLY BEING USED FOR FOAM EXTRUSION. ONE OF THE ESSENTIAL REQUIREMENTS FOR A DIE FOR FOAM POLYSTYRENE IS THAT IT HAVE A STREAMLINE FLOW WITH NO RAPID CHANGES IN CROSS SECTIONAL AREA WITHIN THE FLOW CHANNEL. IN ADDITION,

THE DIE SHOULD HAVE A GRADUALLY DECREASING CROSS SECTIONAL AREA THROUGHOUT THE FLOW CHANNEL TO PREVENT PREMATURE EXPANSION OF THE MELT.

SIZING PLUGS ARE USUALLY CONSTRUCTED OF ALUMINUM AND HAVE PROVISION FOR COOLING TO REMOVE THE FRICTIONAL HEAT GENERATED BY THE MOVING FOAM. BOTH SCORE CUT AND RAZOR BLADE TYPE SLITTERS HAVE BEEN USED SUCCESSFULLY IN CONJUNCTION WITH THE SIZING PLUGS. FIGURES 6 AND 7 SHOW A TYPICAL SIZING PLUG AND A CLOSE-UP OF A SCORE CUT SLITTING ARRANGEMENT.

TWO TYPES OF HAUL-OFF SYSTEMS ARE BEING USED SUCCESSFULLY ON EXISTING FOAM EXTRUSION LINES. FOR THE SIZING PLUG TECHNIQUE, THE EASIEST TO USE IS A DUAL NIP ROLL UNIT CONSISTING OF TWO PAIRS OF RUBBER COVERED PULL ROLLS AND A COMMON DRIVE. THIS SYSTEM OFFERS THE DISADVANTAGE, HOWEVER, OF SLIGHTLY CRUSHING THE FOAM. A MORE REFINED SYSTEM IS AN S-WRAP UNIT THAT IS EQUIPPED WITH A SET OF AUXILIARY NIP ROLLS THAT CAN BE USED TO ASSIST IN STARTING UP THE LINE. WITH BOTH SYSTEMS, LARGE DIAMETER RUBBER COVERED ROLLS ARE USED. FIGURE 8 SHOWS AN S-WRAP PULL ROLL UNIT WITH ADJUSTABLE LEAD-IN IDLER ROLLS TO AID IN PROPER FLATTENING OF THE SHEET. WHEN THE ENTRAPPED AIR TECHNIQUE IS EMPLOYED FOR FILM THICKNESSES OF LESS THAN 20 MILS, A COMBINATION TYPE PULL ROLL UNIT IS USED THAT BOTH COLLAPSES THE TUBE AND SEALS OFF OR ENTRAPS THE AIR IN THE TUBE. THIS UNIT IS SHOWN IN FIGURE 9.

TWO TYPES OF WINDERS HAVE ALSO BEEN SUCCESSFULLY EMPLOYED. SOME CLAIM THAT THE CENTER WINDER WITH EITHER CONSTANT TENSION OR TAPER TENSION CONTROL GIVES THE BEST RESULTS. OTHERS HAVE FOUND THAT EITHER A SINGLE OR DOUBLE DRUM SURFACE WINDER OFFERS SOME DISTINCT ADVANTAGES. IN EITHER CASE, THE WINDER SHOULD BE PROVIDED WITH AN EDGE GUIDE SYSTEM TO INSURE PERFECTLY

STRAIGHT ROLLS. A TYPICAL DUAL TURRET CENTER WINDER IS SHOWN IN FIGURE 10.

SCREW DESIGN

THE PRECEDING EQUIPMENT CONSIDERATIONS CAN SERIOUSLY AFFECT THE QUALITY OF EXTRUDED FOAM POLYSTYRENE SHEET. THE ONE SINGLE FACTOR, HOWEVER, THAT CONTRIBUTES MOST TO THE SUCCESSFUL EXTRUSION OF THIS PRODUCT IS EXTRUDER SCREW DESIGN. IT SHOULD BE KEPT IN MIND THAT, COMPARED TO OTHER THERMOPLASTICS, THE EXTRUSION OF FOAM POLYSTYRENE IS A LOW TEMPERATURE PROCESS. MELT TEMPERATURES AS LOW AS 240°F ARE COMMON. THIS LOW TEMPERATURE PROCESS IS CHARACTERIZED BY THE COMPLETE FOAMING PROCESS TAKING PLACE AS THE EXTRUDATE EMERGES FROM THE DIE AND BY AN EXTRUDED SHEET THAT HAS A UNIFORM UNRUPTURED CELL STRUCTURE AND IS FREE FROM CORRUGATIONS. IN OBTAINING THIS QUALITY LOW TEMPERATURE PROCESS, WE CANNOT, HOWEVER, SACRIFICE SUCH FACTORS AS UNIFORM MIXING AND CONSISTENT SURGE FREE EXTRUSION.

DURING SINCLAIR-KOPPERS' EARLY ATTEMPTS TO DESIGN A SCREW THAT WOULD BE CAPABLE OF PRODUCING QUALITY FOAM SHEET AT OPTIMUM RATES ON A 2-1/2-INCH EXTRUDER, SEVERAL SERIOUS PROBLEMS WERE ENCOUNTERED. PROBABLY THE MOST SIGNIFICANT WAS THE OCCURRENCE OF AREAS OF UNFOAMED POLYSTYRENE SHEET. AT LOW EXTRUSION RATES, A QUALITY SHEET COULD BE PRODUCED; BUT AT HIGHER RATES, THE SHEET CONTAINED UNFOAMED BLOTCHES, AND IN ALL CASES, THE UNFOAMED AREAS WERE ACCOMPANIED BY A LOSS OF PRESSURE IN THE REAR EXTRUDER ZONES. THE PRESSURE PROFILE OBTAINED IS SHOWN IN FIGURE 11.

ANOTHER SERIOUS PROBLEM THAT WAS ENCOUNTERED WAS A SIGN WAVE TYPE FLOW PATTERN IN THE SHEET IN WHICH THE PEAKS ON THE SIGN WAVE CORRESPONDED IDENTICALLY TO THE NUMBER OF SCREW REVOLUTIONS PER MINUTE. THIS PATTERN WAS SO SERIOUS IN SOME INSTANCES THAT IT AFFECTED THE GAGE UNIFORMITY. THE

SCREW PATTERN COULD BE MINIMIZED SOMEWHAT THROUGH THE USE OF A SCREEN PACK, BUT A SCREEN PACK CAUSED EXCESSIVE OVERHEATING OF THE MELT. AFTER MAKING NUMEROUS DESIGN CHANGES, AN EXTRUDER SCREW WAS DEVELOPED THAT ELIMINATED ALL OF THE EARLY PROBLEMS AND WAS CAPABLE OF PRODUCING QUALITY FOAM POLYSTYRENE SHEET AT OPTIMUM EXTRUSION RATES. THE DIMENSIONS OF THIS EXTRUDER SCREW ARE SHOWN IN FIGURE 12. IT HAS A RELATIVELY SHORT YET DEEP FEED SECTION OF 0.500-INCHES, A SHORT TRANSITION SECTION OF 3 FLIGHTS AND A LONG DEEP METERING SECTION OF 17 FLIGHTS AT 0.210-INCHES. ONE SIGNIFICANT CHANGE IN THIS DESIGN IS THAT OF THE NOSE OR SCREW END. THE CONVENTIONAL BREAKER PLATE AND BLUNT SCREW END WAS ELIMINATED AND REPLACED WITH A TAPERED TIP THAT EXTENDED IN THE DIE ADAPTER. THIS NEW SCREW TIP DESIGN IS ILLUSTRATED IN FIGURE 13. THE TOP PORTION SHOWS THE CONVENTIONAL BLUNT SCREW END AND BREAKER PLATE SYSTEM; THE BOTTOM HALF SHOWS THE NEW DESIGN WITH THE BREAKER PLATE ELIMINATED AND THE SCREW END EXTENDED INTO THE DIE ADAPTER. BEST RESULTS WERE OBTAINED BY MATCHING THE ANGLE OF THE SCREW TIP TO THAT OF THE DIE ADAPTER AND BY MAINTAINING THE CLEARANCE BETWEEN THE TIP AND THE ADAPTER EQUAL TO THE METERING DEPTH OF THE SCREW. THIS NEW SCREW DESIGN ELIMINATED THE SIGN WAVE TYPE PATTERN IN THE SHEET AND ALLOWED THE EXTRUSION RATE TO BE INCREASED BY ABOUT 25%. THE MAJOR FACTOR THAT NOW LIMITS THE EXTRUSION RATE ATTAINABLE WITH THIS SCREW DESIGN IS THAT OF COOLING CAPACITY OF THE EXTRUDER.

THE PROCESSING CONDITIONS THAT ARE COMMON FOR FOAM POLYSTYRENE EXTRUSION ARE SHOWN IN FIGURE 14. THESE WERE ESTABLISHED ON A 2-1/2-INCH DIAMETER EXTRUDER USING THE ABOVE SCREW DESIGN.

SHEET PROPERTIES

FIGURE 15 SHOWS SOME TYPICAL PROPERTIES FOR A PIECE OF 50 MIL EXPANDED

POLYSTYRENE SHEET. THE SHEET PROPERTIES AND FACTORS CONTROLLING THESE PROPERTIES THAT ARE OF GREATEST INTEREST HERE, HOWEVER, ARE THOSE WHICH AFFECT THE SUBSEQUENT THERMOFORMABILITY OF THE FOAM SHEET. THESE ARE:

ORIENTATION
CELL SIZE
STIFFNESS
BIAS
EXPANDABILITY

A DETAILED STUDY OF CELL ORIENTATION WOULD IN ITSELF REQUIRE A COMPLETE REPORT. SEVERAL OF THE PROCESSING CONDITIONS THAT INFLUENCE THIS SHEET PROPERTY, HOWEVER, ARE WORTH MENTIONING. OBVIOUSLY, BLOW-UP RATIO, (THE RATIO OF THE PLUG OR TUBE DIAMETER TO THE DIE DIAMETER) PLAYS AN IMPORTANT PART. THE EXTRUSION RATE AND THE DRAW SPEED ALSO HAVE A SIGNIFICANT EFFECT. FIGURES 16, 17, AND 18 WILL ILLUSTRATE THE EFFECT OF THESE THREE PROCESSING CONDITIONS ON CELL ORIENTATION IN THE SHEET. THESE ALL SHOW THE INTERNAL CELL STRUCTURE.

FIGURE 16 IS A PHOTOGRAPH OF A PIECE OF 80 MIL SHEET PRODUCED AT AN EXTRUSION RATE OF 150 POUNDS AN HOUR USING A 7-1/2-INCH DIAMETER DIE AND A 28-INCH DIAMETER SIZING PLUG. THE CELLS IN THIS SHEET ARE ALMOST ROUND AND, IF ANYTHING, SLIGHTLY ELONGATED IN THE TRANSVERSE SHEET DIRECTION. WITH THIS UNIFORM OR ROUND TYPE CELL STRUCTURE, THE SHEET WILL TEND TO LIE FLAT, OR POSSIBLE SHRINK IN BOTH DIRECTIONS WHEN REHEATED IN THE OVEN OF THE THERMOFORMER.

FIGURE 17 IS ALSO A PIECE OF 80 MIL SHEET PRODUCED AT THE SAME EXTRUSION RATE OF 150 POUNDS AN HOUR FROM THE SAME 7-1/2-INCH DIAMETER DIE. IN THIS CASE, HOWEVER, A SMALL 16-3/8-INCH DIAMETER SIZING PLUG WAS USED INSTEAD OF THE 28-INCH DIAMETER PLUG, THUS GIVING A MUCH SMALLER BLOW-UP RATIO. IN THIS CASE, THE CELLS ARE SLIGHTLY ELONGATED IN THE MACHINE DIRECTION. WITH THIS SLIGHT ELONGATION, THE SHEET, WHEN REHEATED IN THE

THERMOFORMER, WILL EXPAND SOMEWHAT IN THE TRANSVERSE DIRECTION, THUS GIVING A SLIGHT WEBBING OR CORRUGATED EFFECT IN THE MACHINE DIRECTION.

FIGURE 18 SHOWS SHEET PRODUCED AT THE SAME EXTRUSION RATE WITH THE SAME DIE AND PLUG COMBINATION. IN THIS CASE THE LINE SPEED WAS INCREASED TO DRAW THE SHEET DOWN FROM A THICKNESS OF 80 MILS TO A THICKNESS OF 40 MILS. THE ELONGATION OF THE CELLS IN THE MACHINE DIRECTION IS MUCH MORE EXAGGERATED IN THIS CASE THEN IT WAS IN FIGURE 17. SHEET OF THIS TYPE, WITH EXCESSIVE ELONGATION IN THE MACHINE DIRECTION, WILL GENERALLY BE UNUSEABLE FOR THERMOFORMING. BECAUSE OF THE EXAGGERATED CONDITION OF ELONGATED CELLS IN THE MACHINE DIRECTION, THE SHEET WILL SHRINK IN THE MACHINE DIRECTION AND EXPAND IN THE TRANSVERSE DIRECTION, THUS PRODUCING A VERY EXTREME CONDITION OF CORRUGATING. THIS CONDITION CAN BE SO SEVERE THAT FOLDS OR OVERLAPPING OF THE SHEET WILL OCCUR WHEN IT IS FORMED. EXTRUDED SHEET THAT IS TO BE USED IN A THERMOFORMING APPLICATION, THEREFORE, SHOULD HAVE A UNIFORM OR ROUND CELL STRUCTURE. EVEN MORE DESIRABLE IS SHEET THAT IS SLIGHTLY STRETCHED OR ORIENTED IN BOTH THE MACHINE AND TRANSVERSE DIRECTIONS.

A SECOND FACTOR AFFECTING THERMOFORMABILITY OF FOAM SHEET, IS THAT OF CELL SIZE. GENERALLY, THE RULE HERE IS THAT THE LARGER THE CELL SIZE, THE MORE EASILY THE SHEET CAN BE FORMED AND THE DEEPER THE DRAWS THAT CAN BE OBTAINED. AS THE CELL SIZE INCREASES, HOWEVER, THE SATINY APPEARANCE AND TEXTURE OF THE FOAM IS LOST AND THE SHEET BECOMES MORE BRITTLE. SO A COMPROMISE MUST BE MAINTAINED BETWEEN THE SHEET AND PART APPEARANCE AND BRITTLINESS, AND THE THERMOFORMABILITY. THE CELL SIZE IS CONTROLLED MAINLY THROUGH THE ADDITIVE OR NUCLEATING SYSTEM IN THE EXTRUSION PROCESS

AND THROUGH THE EXTRUSION CONDITIONS. AN INCREASE IN EITHER OF THE COMPONENTS OF THE NUCLEATING SYSTEM, THAT IS, THE CITRIC ACID OR THE SODIUM BICARBONATE, WILL DECREASE THE CELL SIZE IN THE SHEET. SINCE MOST EXTRUSION GRADE MATERIALS ALREADY CONTAIN THE CITRIC ACID PORTION OF THE NUCLEATING SYSTEM, IT IS ESSENTIALLY THE CONCENTRATION OF THE SODIUM BICARBONATE THAT CONTROLS THE CELL SIZE IN SHEET.

ANOTHER FACTOR AFFECTING THERMOFORMABILITY IS SHEET STIFFNESS. THIS IS MORE DIFFICULT TO CONTROL, HOWEVER, SINCE THE STIFFNESS OF THE EXTRUDED SHEET IS SOMEWHAT DEPENDENT ON THE PROPERTIES OF THE RAW MATERIAL ITSELF. A SLIGHT EFFECT CAN BE REALIZED THROUGH MANIPULATION OF THE EXTRUSION TEMPERATURES: WITHIN LIMITS, THE LOWER THE TEMPERATURES, THE HIGHER THE SHEET DENSITY AND THE STIFFER THE SHEET WILL BE. THE STIFFNESS MAY ALSO BE INCREASED SOMEWHAT THROUGH THE USE OF AN AIR COOLING RING SIMILAR TO THAT USED IN POLYETHYLENE BLOWN FILM EXTRUSION. BLOWING AIR ON THE EXTRUDATE JUST AS IT EMERGES FROM THE DIE LIPS WILL EFFECTIVELY SET UP A HIGH DENSITY SKIN ON THE SHEET SURFACE MAKING THE OVERALL DENSITY HIGHER AND THE SHEET STIFFER. IN BOTH CASES, THE INCREASED DENSITY WILL RESULT IN HIGHER SHEET COSTS.

ANOTHER FACTOR THAT SIGNIFICANTLY AFFECTS THE THERMOFORMABILITY OF FOAM SHEET IS THAT OF BIAS OR EDGES OF UNEQUAL LENGTH. SINCE THE FOAM IS ORIGINALLY EXTRUDED INTO A CIRCULAR FORM, IT IS DIFFICULT TO END UP WITH A PERFECTLY FLAT SHEET. THROUGH PROPER POSITIONING OF THE SLITTING BLADES AND BY INCREASING THE OVERALL LENGTH OF THE EXTRUSION LINE, PARTICULARLY THAT LENGTH BETWEEN THE POINT WHERE THE SHEET IS SLIT AND THE NIP ROLLS, THE FLATNESS AND BIAS CAN BE IMPROVED. IT IS IMPORTANT WHEN SLITTING AT

TWO POINTS TO POSITION THE SLITTING KNIVES SUCH THAT THE DISTANCE FROM THE SLITTING POINTS TO THE PULL ROLLS IS THE SAME FOR BOTH EDGES OF THE SHEET. IF THIS IS NOT DONE, THE BIAS IN THE SHEET WILL MAKE IT DIFFICULT TO HAVE THE SHEET PROPERLY GRIPPED IN THE CHAINS OF THE THERMOFORMING MACHINE. EVEN THOUGH THIS PROCEDURE IS FOLLOWED, HOWEVER, IT CAN BE SHOWN GRAPHICALLY THAT OTHER POINTS ACROSS THE WIDTH OF THE SHEET HAVE NOT TRAVELED THIS SAME DISTANCE BETWEEN THE SLITTING POINT AND THE NIP ROLLS, AND, THEREFORE, ARE OF DIFFERENT LENGTHS THAN THE EDGES. IT CAN ALSO BE SHOWN GRAPHICALLY THAT IT IS MUCH EASIER TO SLIT AT A MINIMUM OF TWO POINTS THAN IT IS TO SLIT AT ONE AND ATTEMPT TO FLATTEN THE ENTIRE CIRCUMFERENCE.

THE FINAL IMPORTANT SHEET PROPERTY AFFECTING THERMOFORMABILITY IS THE EXPANDABILITY OF THE SHEET. ORIENTATION, DENSITY, AND THICKNESS, ALL SLIGHTLY INFLUENCE THE EXPANDABILITY.

SHEET AGE, HOWEVER, IS THE MOST IMPORTANT CONSIDERATION. FIGURE 19 SHOWS A PLOT OF THE SHEET AGE IN DAYS VERSUS THE PERCENT OF EXPANSION, THAT IS, PERCENT OF THE ORIGINAL SHEET THICKNESS. OBVIOUSLY, THE FIRST TWO DAYS IS NOT THE PROPER TIME TO THERMOFORM FOAM SHEET. AFTER THE SECOND DAY, HOWEVER, THE CURVE LEVELS OFF. IN ADDITION TO EXPANDABILITY ALONE, IT HAS RECENTLY BEEN FOUND THAT THE OLDER THE SHEET THE BETTER THE OVERALL THERMOFORMABILITY. THIS EFFECT OF SHEET AGE ON EXPANDABILITY AND THERMOFORMABILITY IS ALSO A STRONG ARGUMENT AGAINST SETTING UP AN INLINE EXTRUSION AND THERMOFORMING OPERATION.

THE THERMOFORMING PROCESS

THE MAJORITY OF PARTS CURRENTLY BEING THERMOFORMED FROM FOAM SHEET, INCLUDING THOSE STILL IN THE PROTOTYPE STAGE, ARE LARGE VOLUME ITEMS THAT REQUIRE THE USE OF A CONTINUOUS ROLL FED THERMOFORMING MACHINE. ITEMS SUCH

AS MEAT TRAYS, EGG CARTONS, PRODUCE TRAYS, AND APPLE SHIPPING TRAYS ARE QUITE COMMON, WHEREAS LARGE, DEEP DRAW PARTS USUALLY ASSOCIATED WITH ROTARY OR SHEET FEED MACHINES ARE ALMOST NON-EXISTENT. THIS DISCUSSION OF THE THERMOFORMING PROCESS, THEREFORE, WILL BE LIMITED STRICTLY TO ROLL FED OR CONTINUOUS MACHINES, ALTHOUGH SOME OF THE TECHNIQUES USED HERE ARE CERTAINLY APPLICABLE ON SHEET FED THERMOFORMERS. FIGURES 20 AND 21 SHOW TWO TYPICAL CONTINUOUS THERMOFORMERS.

THE TECHNIQUES AND PRINCIPLES THAT APPLY TO THE FORMING OF OTHER THERMOPLASTICS CERTAINLY HOLD TRUE FOR FOAM, BUT, BECAUSE OF THE LOW DENSITY, HEAT SENSITIVITY, RAPID COOLING, AND LOW ELONGATION OF THE FOAM SHEET, THE PROBLEMS GENERALLY ASSOCIATED WITH THE THERMOFORMING OF OTHER MATERIALS ARE MAGNIFIED.

THE HEATING PORTION OF THE THERMOFORMING PROCESS IS PROBABLY THE MOST CRITICAL PHASE. THE FORMING TEMPERATURE RANGE FOR FOAM SHEET IS VERY NARROW. THERE ARE ONLY A FEW TENTHS OF A SECOND BETWEEN THE TIME THAT SHEET IS PLIABLE ENOUGH TO BE FORMED INTO THE CONTOUR OF A MOLD AND THE TIME THAT THE SHEET IS OVERHEATED AND THE CELL STRUCTURE IS COMPLETELY BROKEN DOWN. IN ALMOST ALL CASES, THE OPTIMUM COMBINATION OF FORMING TEMPERATURES AND FORMING TIME RESULTS IN A SHEET WHICH HAS ACHIEVED THE MAXIMUM ATTAINABLE EXPANSION. FURTHER HEATING OF THE SHEET RESULTS IN A SLIGHT BREAK DOWN OR GLOSSY APPEARANCE TO THE SHEET SURFACE, AND A RESULTANT LOSS OF THICKNESS AND INCREASE IN DENSITY. ON THE OTHER HAND, WHEN THE MAXIMUM EXPANSION POINT HAS NOT BEEN REACHED THE SHEET IS NORMALLY TOO COLD TO FORM, AND TEARING WILL RESULT. THEREFORE, THE SHEET EXPANSION IS USED AS A GUIDE FOR DETERMINING THE PROPER COMBINATION OF CYCLE AND TEMPERATURE.

IN ALMOST ALL CASES, TWO SIDED OR SANDWICH TYPE HEATING IS A MUST. ALTHOUGH IT IS POSSIBLE WITH SINGLE SIDED HEATING TO FORM PARTS WITH SHALLOW DRAWS AND LARGE RADIUS THE BEST CONTROL AND BEST FORMING EFFICIENCY CAN ONLY BE REALIZED IF TWO SIDED HEATING IS USED. THIS IS PARTICULARLY TRUE FOR SHEET THICKNESSES ABOVE 50 MILS. FOR THESE THICKER GAUGES, IT IS VIRTUALLY IMPOSSIBLE WITH SINGLE SIDED HEATING TO OBTAIN THE OPTIMUM FORMING TEMPERATURE THROUGHOUT THE ENTIRE THICKNESS OF THE SHEET.

ON MOST THERMOFORMERS THAT ARE MANUFACTURED FOR POLYSTYRENE FOAM SHEET, RADIANT TYPE HEATERS ARE USED. IN SOME CASES, HEATING ELEMENTS ARE SUPPLIED THAT ARE SHIELDED WITH A FUSED QUARTZ PANEL TO MORE UNIFORMLY DISTRIBUTE THE HEAT. WHATEVER THE TYPE OF HEATING SYSTEM USED, HOWEVER, THE MOST IMPORTANT FACTOR IS UNIFORM HEAT DISTRIBUTION AND GOOD TEMPERATURE CONTROL. WITH NON-UNIFORM HEAT IT IS POSSIBLE TO OVERHEAT THE SHEET IN SOME AREAS AND STILL HAVE IT TOO COLD TO FORM IN OTHER AREAS. OBVIOUSLY, THE GREATER THE DISTANCE OF THE HEATING ELEMENTS FROM THE SHEET THE MORE UNIFORM THE HEAT DISTRIBUTION WILL BE. IN ORDER TO MINIMIZE LOCALIZED OVERHEATING, WITH THE RADIANT TYPE HEATERS, THE ELEMENTS SHOULD BE AT LEAST 4 INCHES AWAY FROM THE SHEET AND PREFERABLY 12 INCHES AWAY. THE TEMPERATURE OF THE HEATING ELEMENT IS MOST ACCURATELY CONTROLLED WITH EITHER PROPORTIONING OR STEPLESS TEMPERATURE CONTROL INSTRUMENTS WITH THE SENSING THERMOCOUPLE MOUNTED DIRECTLY ON THE HEATING ELEMENT. IN ADDITION TO THE HEATING ELEMENTS THAT RUN PERPENDICULAR TO THE TRAVEL OF THE SHEET THROUGH THE OVEN, AUXILIARY HEATERS MAY BE USED TO COMPENSATE FOR THE RAPID COOLING OF THE FOAM SHEET. EDGE HEATERS TAKE CARE OF HEAT LOSSES THROUGH THE SIDES OF THE OVEN AND LOSSES THROUGH CONDUCTION TO THE CHAIN OR GRIPPING MECHANISM, WHILE ADDITIONAL HEATERS INSTALLED NEAR THE FRONT END OF THE OVEN TAKE CARE OF HEAT LOSSES AS

THE SHEET MOVES FROM THE OVEN INTO THE MOLD.

FORMING TECHNIQUES

THE MOST WIDELY USED METHODS FOR FORMING FOAM POLYSTYRENE SHEET ARE THE VERY SIMPLE TECHNIQUES OF VACUUM FORMING OVER A MALE MOLD OR VACUUM FORMING INTO A FEMALE MOLD. IN MANY CASES, A PLUG ASSIST OR PRE-PLUGGING TECHNIQUE IS ALSO USED.

FORMING OVER A MALE MOLD OR INTO A FEMALE MOLD CONSISTS BASICALLY OF MOVING THE SHEET OUT OF THE OVEN AND INTO THE AREA IMMEDIATELY ABOVE OR BELOW THE MOLD. THE MOLD AND EITHER A SEAL RING OR PRESSURE BOX THEN CLOSE ON THE SHEET AND FORM A SEAL AROUND THE OUTER PERIMETER OF THE MOLD. A VACUUM IS THEN DRAWN, PULLING THE SHEET TO CONFORM TO THE CONTOUR OF THE MOLD. THE SHEET REMAINS IN THIS POSITION UNTIL IT IS SUFFICIENTLY COOLED. THE MOLD AND SEAL RING THEN SEPARATE AND THE PROCESS IS REPEATED. THIS IS THE BASIC TECHNIQUE USED FOR THERMOFORMING SHALLOW DRAW PARTS SUCH AS MEAT TRAYS OR APPLE TRAYS. A SIX CAVITY MEAT TRAY MOLD, MOUNTED IN A CONTINUOUS FORMING MACHINE IS SHOWN IN FIGURE 22. THE DRAW RATIO IS LIMITED TO ABOUT 0.5:1 FOR FOAM SHEET WHEN USING THIS TECHNIQUE WITHOUT A PLUG ASSIST. DRAW RATIO HERE IS DEFINED AS THE RATIO OF THE HEIGHT OR DEPTH OF THE PART TO THE SMALLEST DIMENSION OF ITS OPENING. SLIGHTLY DEEPER DRAWS REQUIRE THE USE OF A PLUG ASSIST OR PRE-PLUGGING OPERATION USED IN CONJUNCTION WITH EITHER A MALE OR FEMALE MOLD TO HELP PRE-STRETCH OR FORCE THE SHEET INTO THE MOLD CAVITY. WITH A PLUG ASSIST DRAW RATIOS AS HIGH AS 1:1 CAN BE OBTAINED PROVIDED THAT THE PART HAS LARGE DRAFT ANGLES AND LARGE RADII.

AN EXAMPLE OF PLUG ASSIST FORMING IS THE HOT DRINK OR VENDING CUP. IN THIS TECHNIQUE THE SHEET IS FIRST CLAMPED OVER THE FEMALE MOLD. THE PLUG

THEN ENTERS THE SHEET, FORCING IT DOWN INTO THE MOLD CAVITY. AS THE PLUG ENTERS THE MOLD, THE RATE AT WHICH THE AIR IS EVACUATED FROM THE MOLD IS CONTROLLED AND THIS ALSO CONTROLS THE DISTRIBUTION OF THE SHEET WITHIN THE MOLD. FIGURE 23 SHOWS CUPS BEING FORMED BY THE PLUG ASSIST TECHNIQUE ON A NINE CAVITY MOLD.

EVEN THOUGH A PLUG ASSIST OR PRE-PLUGGING OPERATION IS NOT NORMALLY REQUIRED FOR SIMPLE DRAWS, SOME ADDITIONAL ADVANTAGE CAN OFTEN BE OBTAINED BY USING A PLUG ASSIST OR EVEN A MATCHED PLUG. MEAT TRAYS HAVE BEEN FORMED FROM FOAM SHEET USING JUST A FEMALE MOLD AND NO PLUG ASSISTS ON A 3 SECOND OVERALL CYCLE. BY USING A MATCHED PLUG ASSIST, WITH THE FEMALE MOLD, ADDITIONAL COOLING CAPACITY IS OBTAINED ON THE OPPOSITE SIDE OF THE SHEET AND THE OVERALL CYCLE CAN BE REDUCED TO 2-1/2 SECONDS. SINCE THE FOAM CAN BE VERY EASILY CRUSHED A PLUG ASSIST OR MATCHED PLUG CAN ALSO BE USED TO ACCURATELY CONTROL THE THICKNESS OF THE FOAMED PART IN ANY PARTICULAR AREA. ON A MEAT TRAY AGAIN, IT IS POSSIBLE BY USING A MATCHED PLUG ASSIST TO REDUCE THE OVERALL FORMING CYCLE AND TO ACCURATELY CONTROL THE THICKNESS OF THE BOTTOM OF THE TRAY, EVEN THOUGH THIS PLUG ASSIST WOULD NOT NORMALLY BE REQUIRED FOR SUCH A SHALLOW DRAW. WHEN SHARP DETAIL IS REQUIRED ON BOTH SIDES OF THE THERMOFORMED PART, THE PLUG ASSIST AND A SLIGHT COMPRESSING TECHNIQUE CAN ALSO BE USED TO ADVANTAGE. NORMALLY, BECAUSE OF THE EXPANDED THICKNESS AND TEXTURE OF FOAM SHEET, SHARP DETAIL CAN ONLY BE OBTAINED ON THAT SIDE OF THE SHEET THAT COMES IN CONTACT WITH THE MOLD. BY SLIGHTLY COMPRESSING THE SHEET ON THE OPPOSITE SIDE WITH A PLUG, SHARP DETAIL MAY BE OBTAINED ON BOTH SIDES

PART DESIGN

DEPTH RATIO AGAIN IS THE RATIO OF THE DEPTH OF THE THERMOFORMED PART

TO THE NARROWEST DIMENSION OF ITS OPENING. AS A GENERAL RULE, A 1:1 DRAW RATIO IS THE LIMIT FOR LOW DENSITY FOAM POLYSTYRENE, AND THIS ONLY UNDER THE IDEAL CONDITIONS OF A LARGE DRAFT ANGLE AND LARGE RADII. THESE RATHER SEVERE DRAW LIMITATIONS MUST BE KEPT IN MIND WHEN DESIGNING A PART OR MOLD FOR FOAM SHEET. GENERALLY, THE PART SHOULD BE KEPT AS STREAMLINED AS POSSIBLE. A MINIMUM DRAFT ANGLE OF 10 TO 15 DEGREES IS DESIRABLE AND LARGE ANGLES NOT ONLY MAKE THE PART EASIER TO FORM BUT ALSO AID IN THE SUBSEQUENT STACKING OF THE TRIM PARTS. ALSO THE RADII SHOULD BE AT LEAST AS LARGE AS THE THICKNESS OF THE SHEET BEING FORMED. OTHER RULES THAT APPLY TO THE DESIGNING OF PARTS TO BE THERMOFORMED FROM POLYSTYRENE, POLYETHYLENE, AND OTHER THERMOPLASTICS ALSO APPLY TO FOAM SHEET. RIGIDITY AND STRUCTURAL STRENGTH SHOULD BE DESIGNED INTO THE FORMED PIECE THROUGH THE USE OF RIBS, CORRUGATIONS, AND CURVED OR DOMED SURFACES, AND UNDERCUTS SHOULD BE AVOIDED, IF AT ALL POSSIBLE.

FORMING CONDITIONS

IN SELECTING A PROPER COMBINATION OF FOAM SHEET PROPERTIES, PARTICULARLY THICKNESS AND DENSITY, COST IS OBVIOUSLY THE MOST IMPORTANT CONSIDERATION. BUT THE FORMING LIMITATIONS AND OTHER SHEET PROPERTIES SUCH AS EXPANDABILITY MUST ALSO BE KEPT IN MIND. AS DISCUSSED EARLIER, FOAM SHEET WHEN HEATED, EXPANDS TO APPROXIMATELY TWICE ITS ORIGINAL THICKNESS. IT IS THIS EXPANDED THICKNESS, PARTICULARLY IN SHALLOW DRAW PARTS, THAT SHOULD BE CONSIDERED WHEN SPECIFYING THE SHEET CHARACTERISTICS. IN SOME CASES WHEN RELATIVELY DEEP DRAWS OF 0.8:1 OR GREATER ARE ANTICIPATED, IT MAY BE NECESSARY TO USE A SLIGHTLY HIGHER DENSITY SHEET, EVEN THOUGH THIS HIGHER DENSITY WILL INCREASE THE UNIT COST. GENERALLY SPEAKING, HOWEVER, FOR REASONS OF BOTH ECONOMY AND STRUCTURAL STRENGTH IN THE FORMED PART, IT IS BEST TO SELECT THE LOWEST POSSIBLE DENSITY AND LET THE SHEET THICKNESS BE THE DETERMINING FACTOR.

AFTER THE SHEET HAS BEEN SELECTED, THE NEXT STEP IS TO DETERMINE THE OPTIMUM PROCESSING CONDITIONS. ESSENTIALLY THIS MEANS DETERMINING THE SHORTEST TIME CYCLE AT WHICH A QUALITY PART CAN BE MADE. BECAUSE OF THE INSULATING PROPERTIES OF THE FOAM, HIGH TEMPERATURES AND SHORT CYCLE TIMES OFTEN RESULT IN A SHEET THAT HAS BEEN OVERHEATED AND BROKEN DOWN ON THE OUTSIDE SURFACES, YET IS TOO COLD TO FORM ON THE INSIDE. SOME COMPROMISE MUST, THEREFORE, BE ACHIEVED BY LOWERING THE HEATER TEMPERATURES AND LENGTHENING THE CYCLE TO OBTAIN A SHEET WHICH IS HEATED AS UNIFORMLY AS POSSIBLE THROUGHOUT. NORMALLY 1200°F IS CONSIDERED THE MAXIMUM HEATER TEMPERATURE AND 500°F THE MINIMUM. THE PART DESIGN AND SHEET THICKNESS DETERMINE WHAT COMBINATION OF TEMPERATURE AND CYCLE TIME CAN BE USED. FOR SHALLOW DRAWS AND RELATIVELY THIN SHEET, HIGH TEMPERATURES AND SHORT CYCLE TIMES MAY BE USED. FOR MORE CRITICAL DRAWS AND THICKER SHEET, HOWEVER, A LONGER CYCLE AND LOWER TEMPERATURES ARE REQUIRED. TYPICAL FORMING CONDITIONS FOR 60 MIL SHEET AND A RELATIVELY SHALLOW DRAW ARE LISTED IN FIGURE 24.

ALTHOUGH FOAM SHEET COOLS VERY RAPIDLY COMPARED TO OTHER THERMOPLASTIC SHEET MATERIALS, THE COOLING PORTION OF THE THERMOFORMING CYCLE IS STILL EXTREMELY CRITICAL. INSUFFICIENT COOLING TIME WILL RESULT IN WARPED OR DISTORTED FOAM PARTS JUST AS IT WILL WITH PARTS FORMED FROM POLYETHYLENE. IN MOST CASES, THE MOLD TEMPERATURES SHOULD BE KEPT AS COLD AS POSSIBLE, AND PARTICULAR ATTENTION SHOULD BE GIVEN TO THE MOLD DESIGN TO INSURE GOOD COOLING AROUND THE PERIMETER OF EACH OF THE MOLD CAVITIES. IN SOME CASES, HOWEVER, THE MOLD IS HEATED SLIGHTLY TO AID IN SHEET DISTRIBUTION. GENERALLY, WITH THE MORE EFFICIENT AND FASTER CONTINUOUS THERMOFORMING MACHINES, THE COOLING CYCLE, REPRESENTS, BY FAR, THE GREATEST PERCENTAGE OF THE OVERALL FORMING CYCLE. EVEN THOUGH COMPLETE AND EFFICIENT COOLING OF THE THERMOFORMED PART IS

ACHIEVED, HOWEVER, SOME SHRINKAGE WILL STILL TAKE PLACE DURING THE TIME THAT THE FORMED PART AND WEB PASS FROM THE MOLD TO THE TRIMMING STATION. BECAUSE THE DEGREE OF SHRINKAGE IS DEPENDENT NOT ONLY ON COOLING EFFICIENCY, BUT ALSO ON THE DESIGN AND CONFIGURATION OF THE FORMED PART, IT IS IMPOSSIBLE TO SET A DEFINITE FIGURE SHRINKAGE VALUE. BEST ESTIMATES OF THIS PROPERTY, HOWEVER, SHOW THAT THE SHRINKAGE IS USUALLY OF THE ORDER OF 0.008 INCHES PER INCH.

TRIMMING

SEVERAL TRIMMING TECHNIQUES HAVE BEEN USED SUCCESSFULLY FOR FOAM POLYSTYRENE SHEET. BEST RESULTS ARE USUALLY ACHIEVED WITH MATCHED METAL DIES AND A SHEAR CUTTING ARRANGEMENT. THIS TECHNIQUE, HOWEVER, REQUIRES AN EXPENSIVE TRIMMING PRESS, AND RESULTS IN HIGH TOOLING COSTS. A TYPICAL TRIM PRESS FOR USE WITH MATCHED METAL DIES IS SHOWN IN FIGURE 25. WHEN THE ENTIRE CUT OR TRIM IS TO BE MADE IN THE SAME PLANE A CIRCULAR OR BAND SAW CAN BE USED. WITH THIS PROCESS, HOWEVER, NO PROTRUSIONS CAN BE PRESENT IN THE FORMED PART THAT WILL INTERFERE WITH THE SAW BLADE. FOR SHORT RUNS, STEEL RULE DIES DO AN EXCELLENT JOB AND ARE INEXPENSIVE. THE NEWEST TECHNIQUE FOR FOAM CONSISTS OF TRIMMING THE THERMOFORMED PART RIGHT IN THE MOLD. THIS RESULTS IN SLIGHTLY HIGHER MOLD COSTS, BUT ELIMINATES THE NEED FOR AN EXPENSIVE TRIMMING PRESS OR SAW. IT ALSO MEANS THAT SHRINKAGE OF THE PART OR WEB NEED NOT BE CONSIDERED WHEN SIZING THE TRIMMING DIES.

ACKNOWLEDGEMENTS

FIGURES 1, 4, 6, 7, 8, 9, AND 10 WERE REPRODUCED THROUGH THE COURTESY OF NORTHEAST PLASTIC MACHINERY CO., INC., MANCHESTER, NEW HAMPSHIRE. FIGURES 21 AND 25 WERE REPRODUCED THROUGH THE COURTESY OF KIRKHOF MFG. CORP., GRAND RAPIDS, MICHIGAN. ALL OTHER PHOTOGRAPHS, TABLES, AND GRAPHS WERE PREPARED IN THE PRODUCT DEVELOPMENT LABORATORIES OF SINCLAIR-KOPPERS CO.

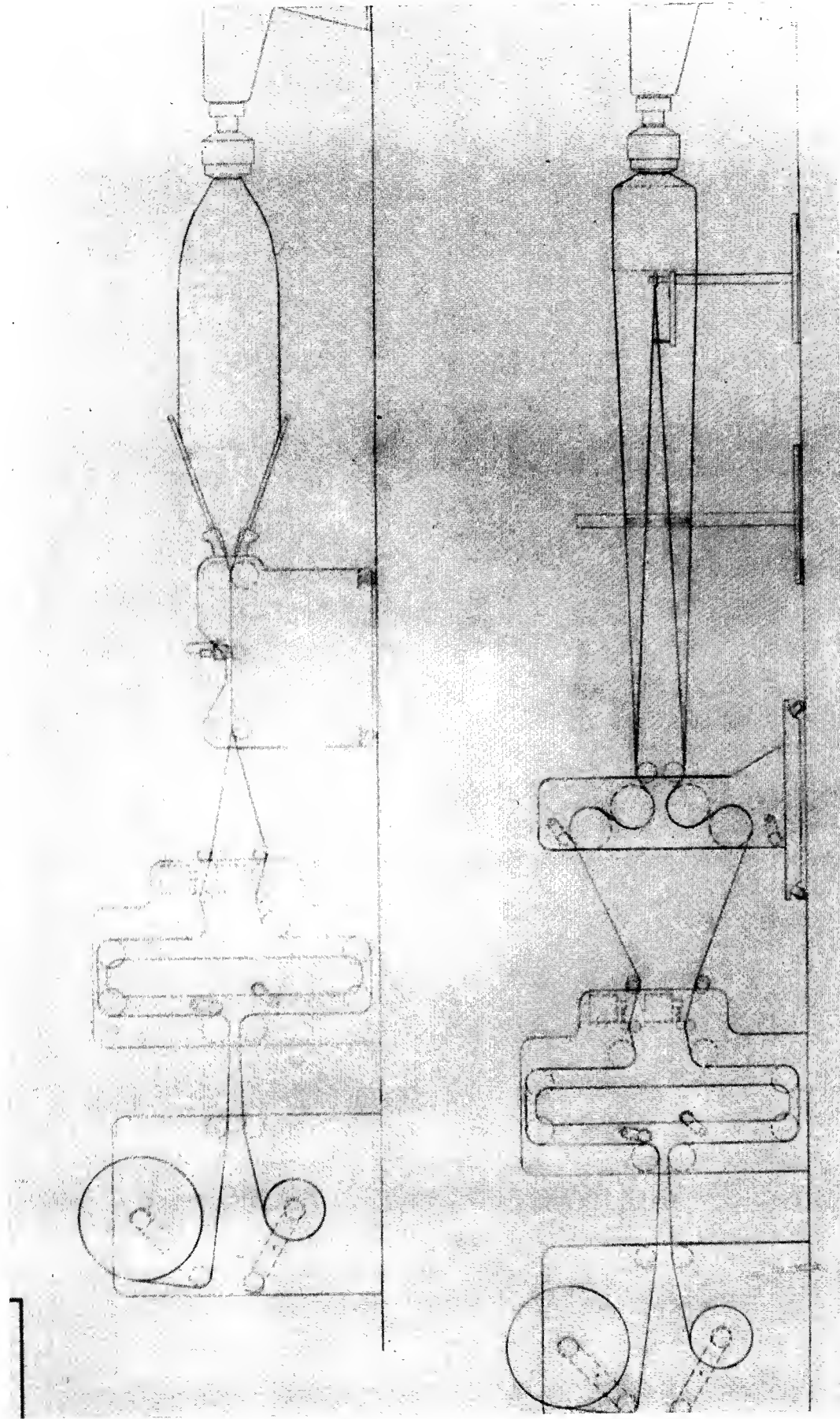


Figure 1.

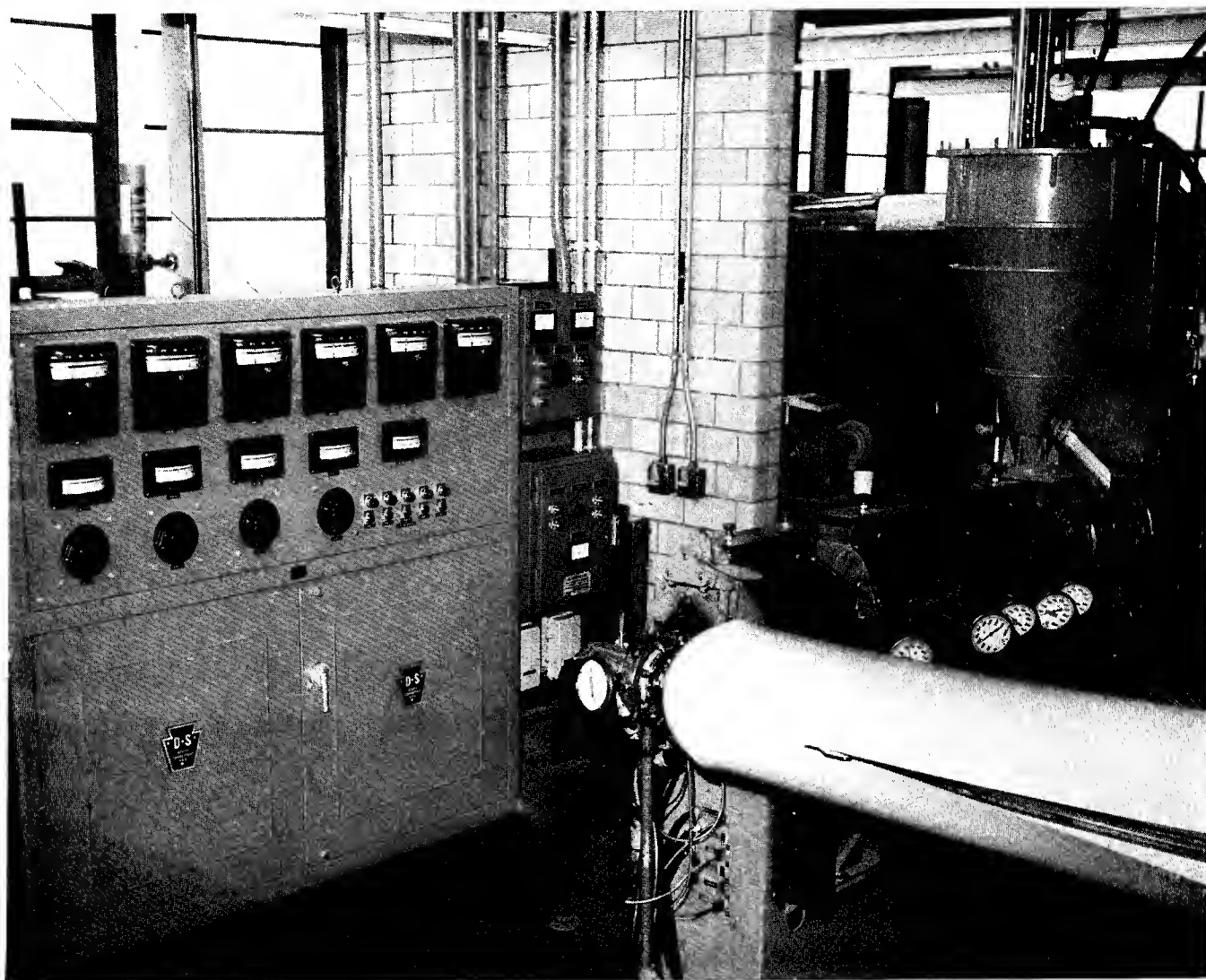


Figure 2.

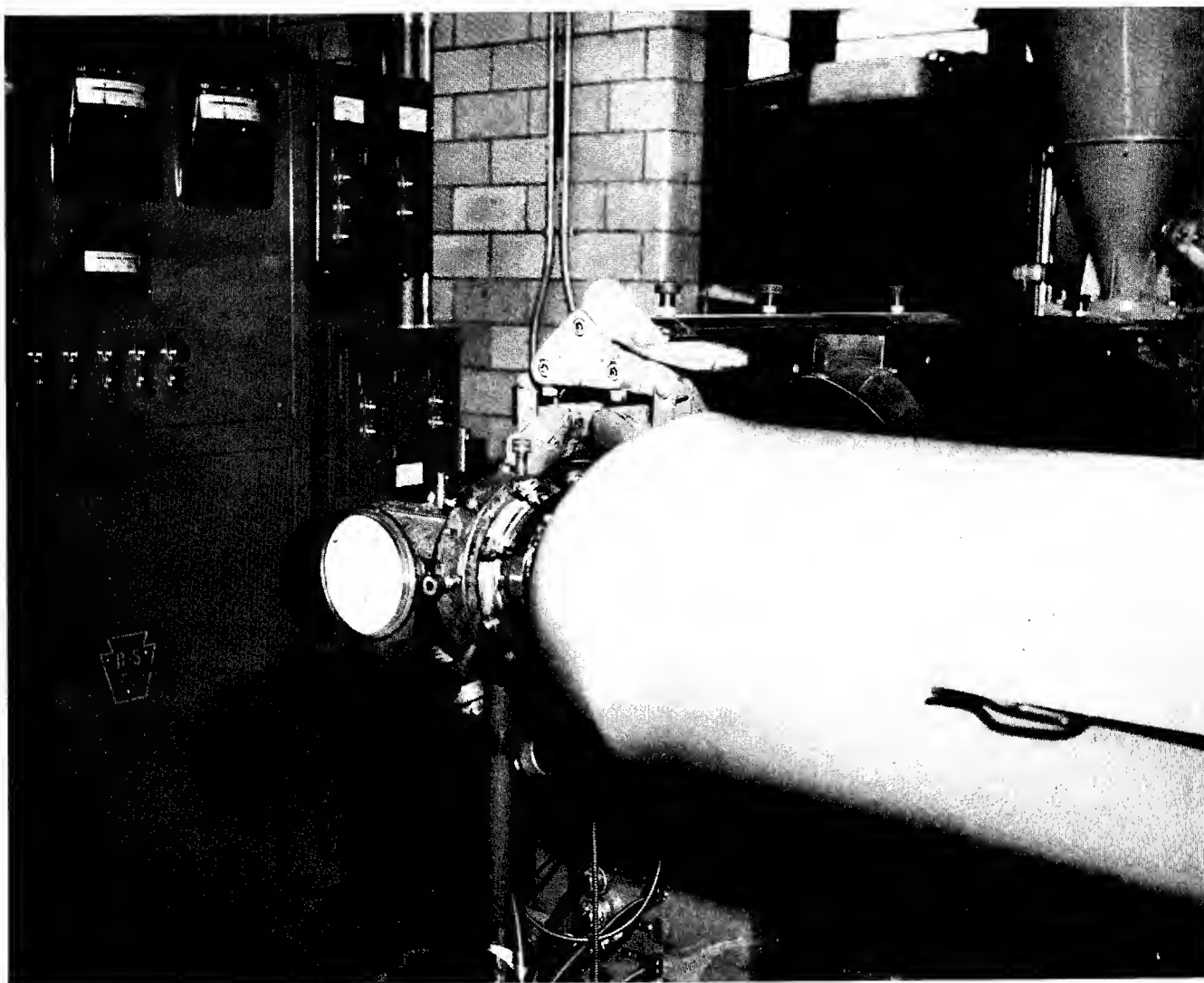


Figure 3.



Figure 4.



Figure 5.

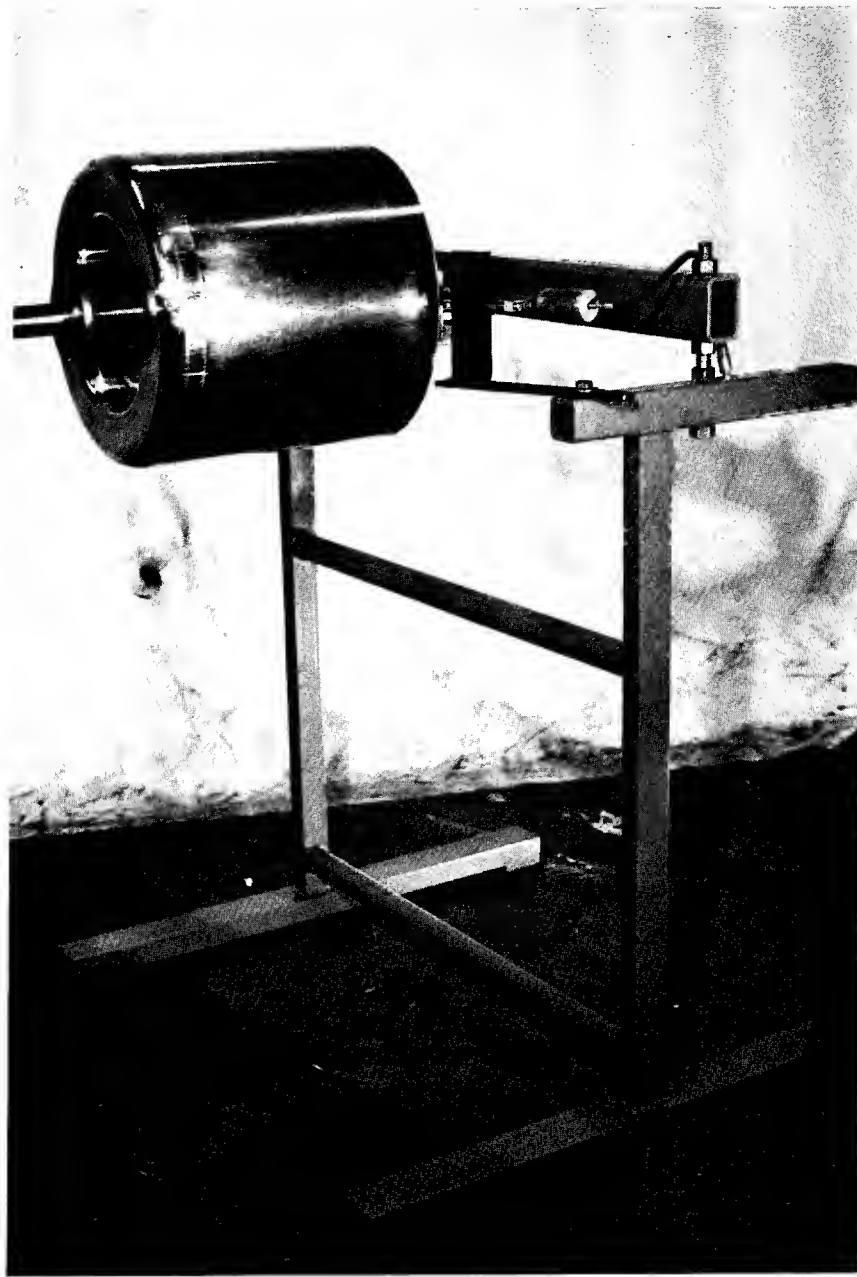


Figure 6.

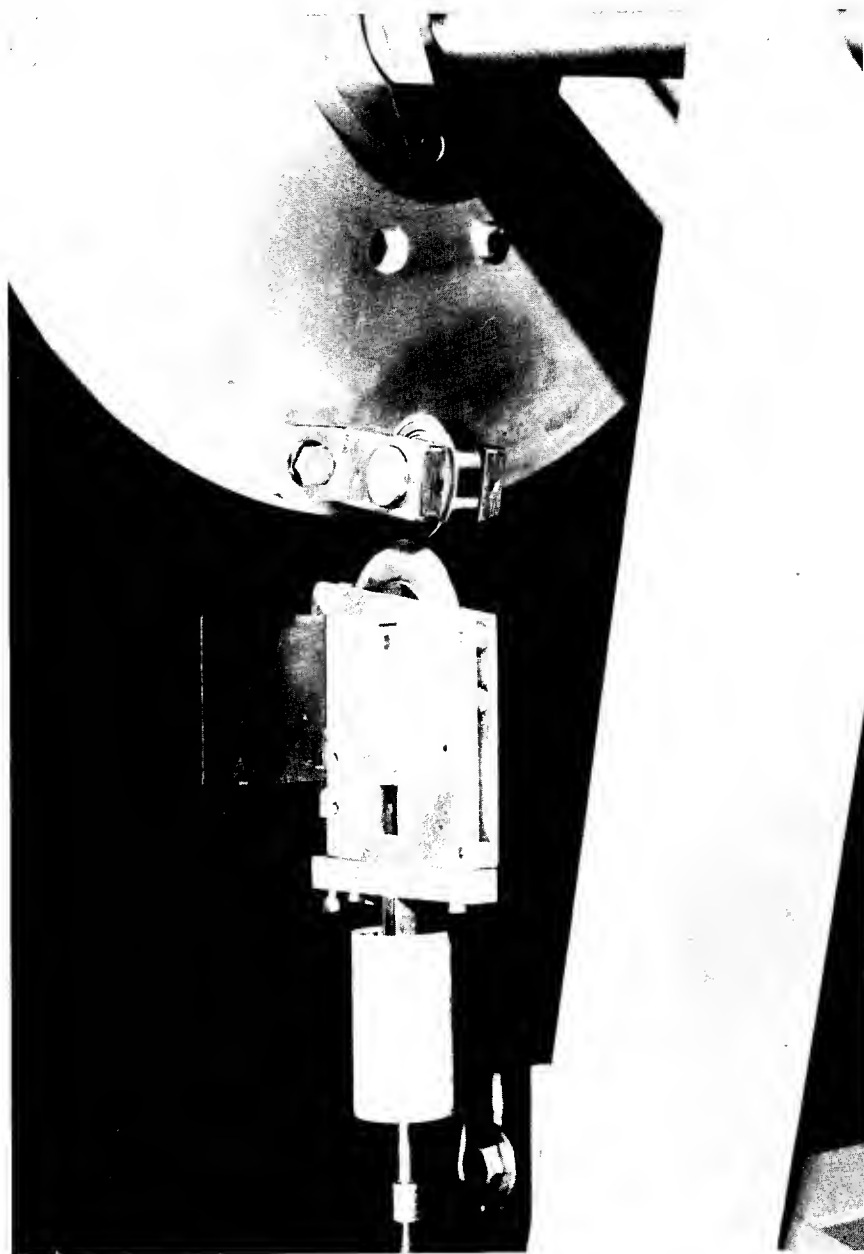


Figure 7.

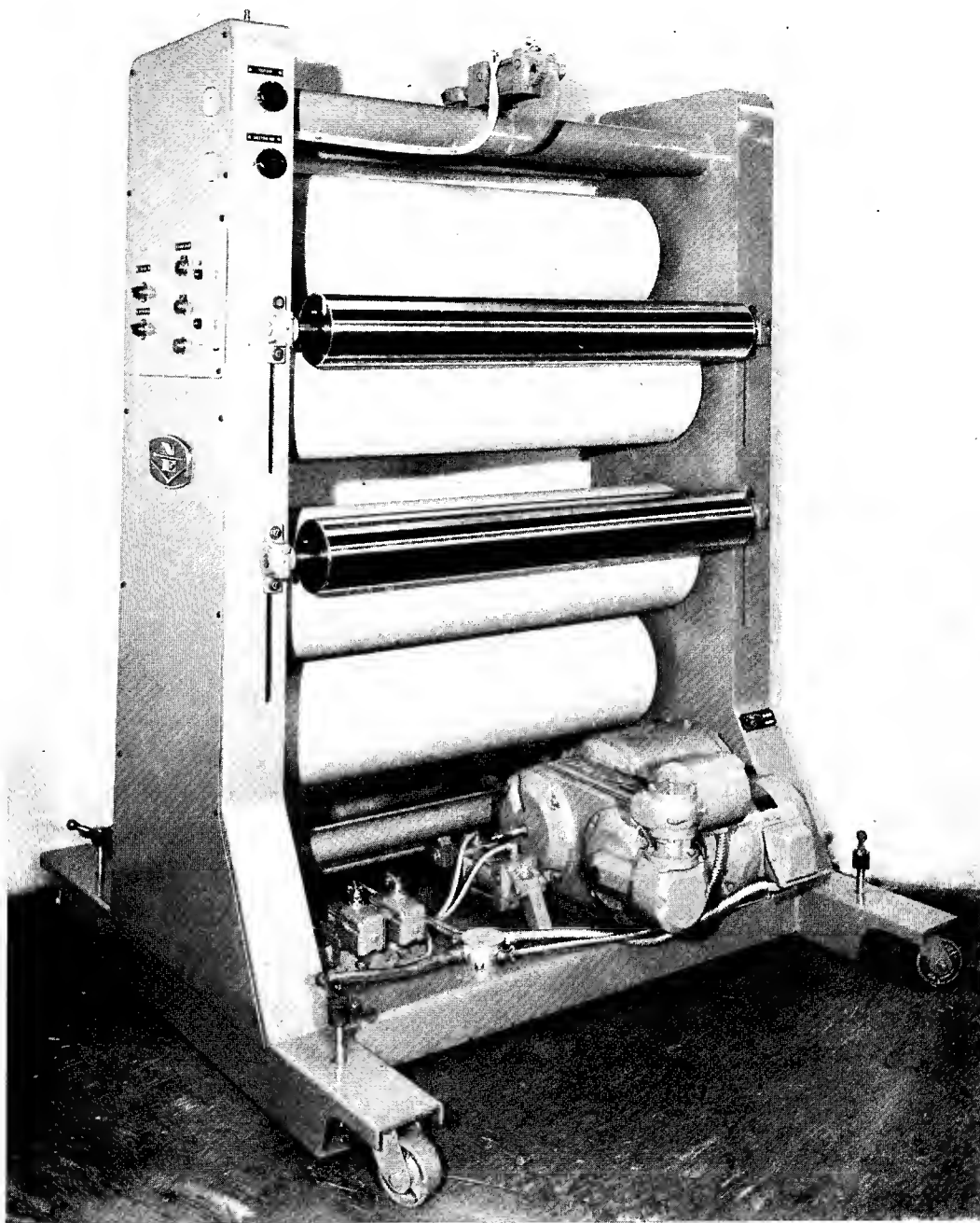


Figure 8.

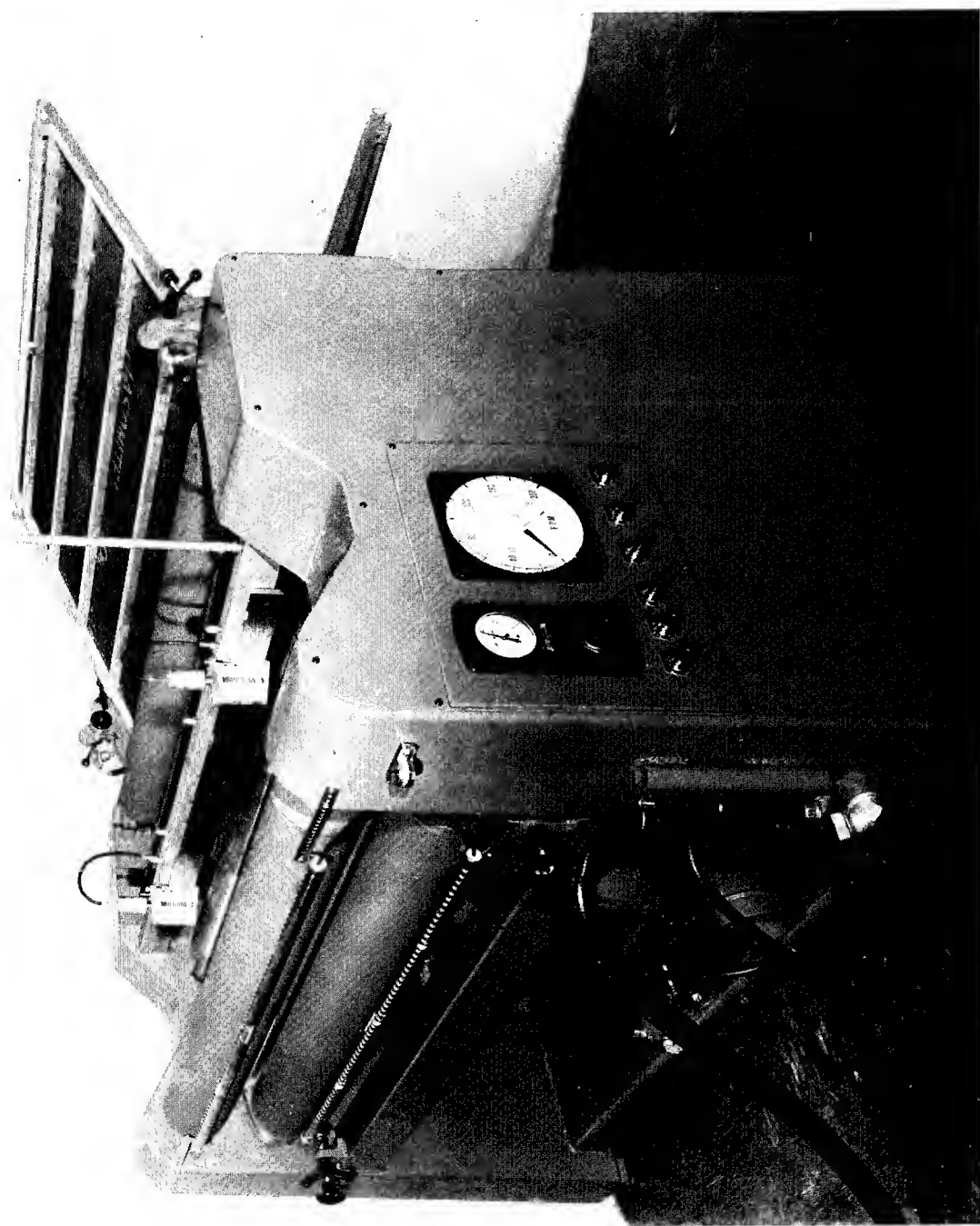


Figure 9.

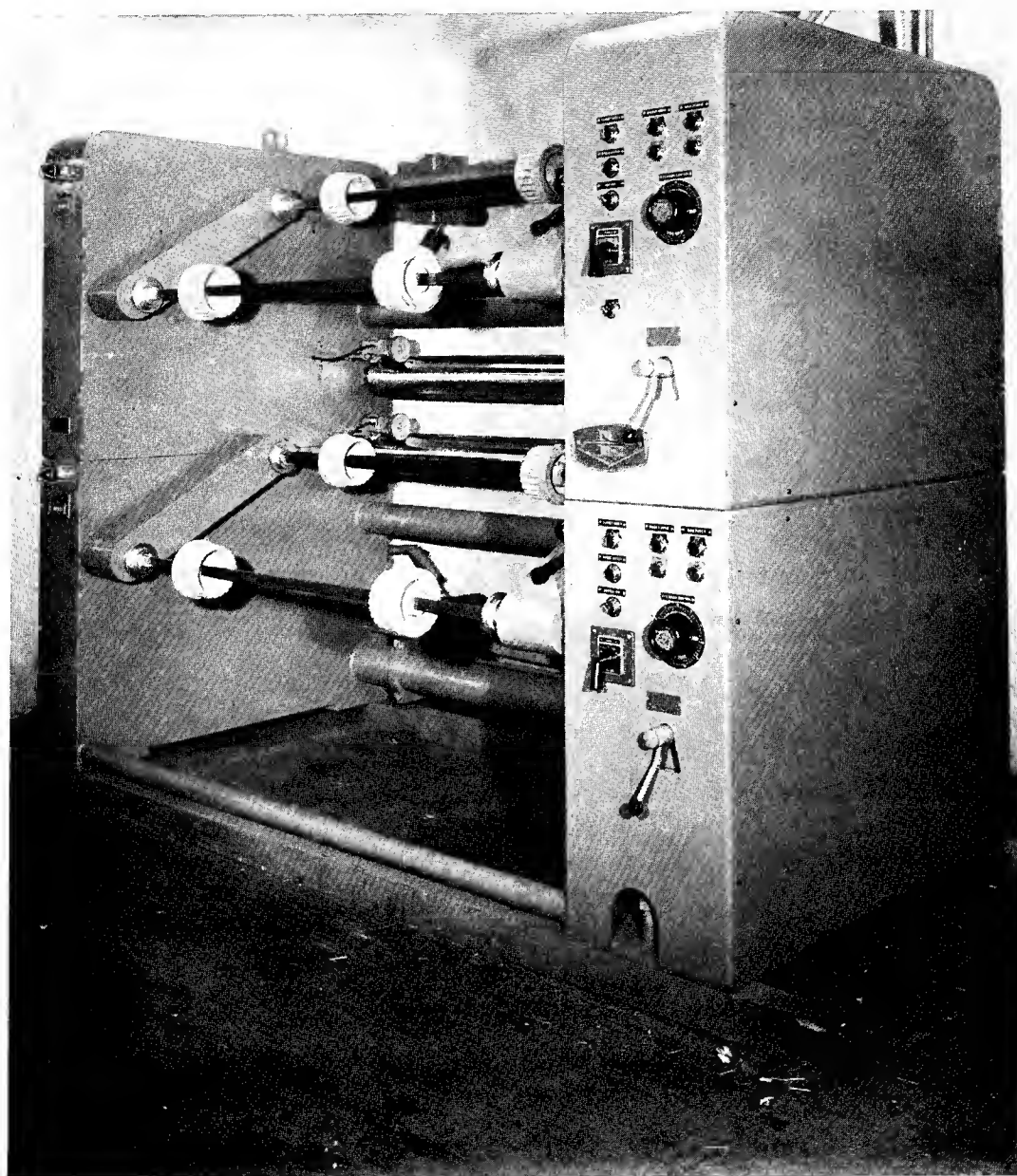


Figure 10.

PRESSURE PROFILE
ORIGINAL SCALE UP

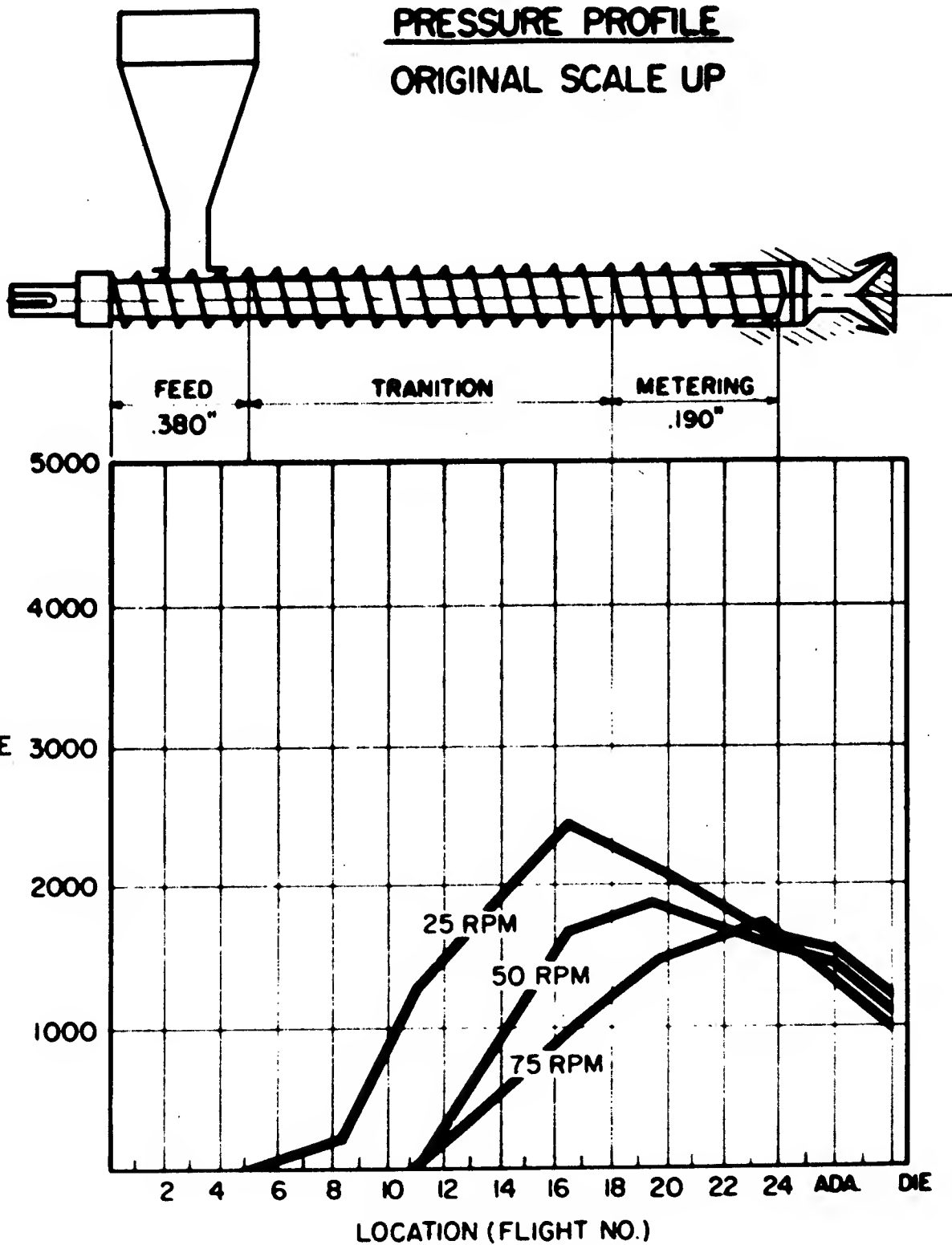
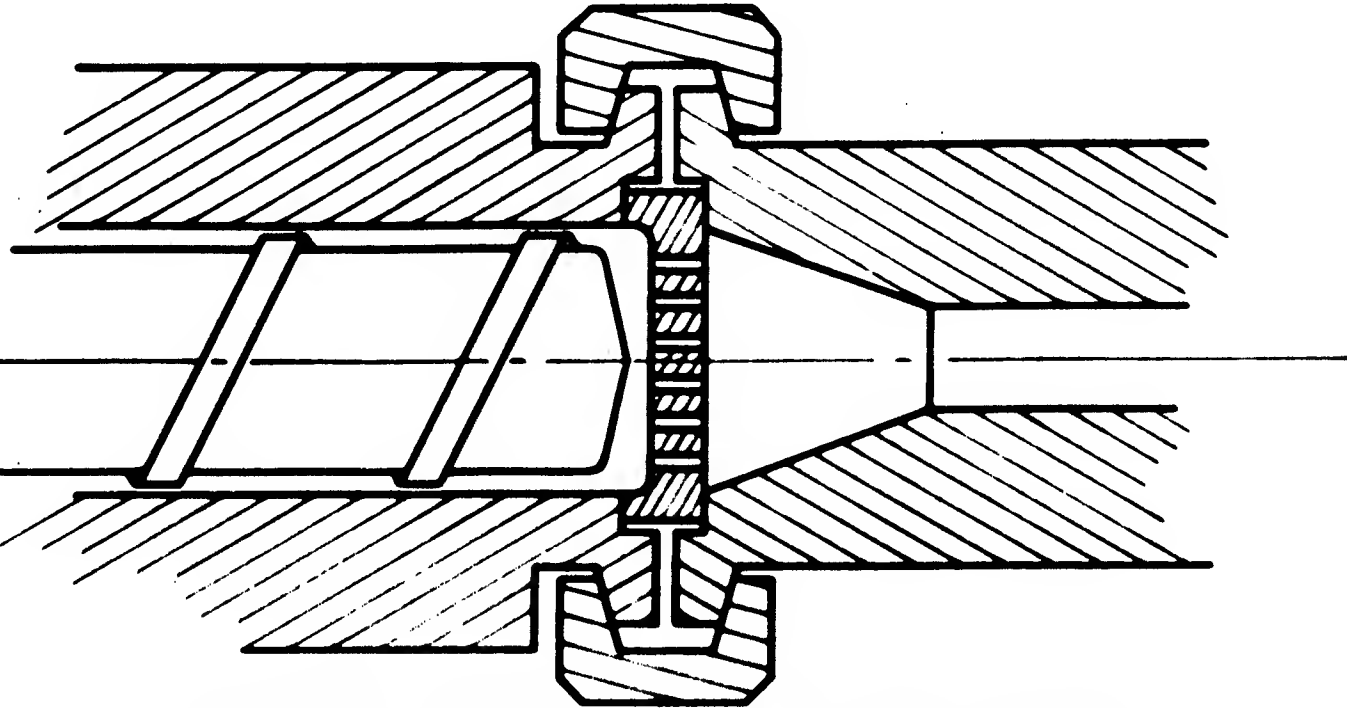


Figure 11.

<u>SCREW DIMENSIONS</u> <u>FOR 2-1/2-INCH DIAMETER EXTRUDER</u>		
FEED DEPTH	—	0.500"
FEED LENGTH	—	4 FLIGHTS
TRANSITION	—	3 FLIGHTS
METERING LENGTH	—	17 FLIGHTS
METERING DEPTH	—	0.210"
FRONT NOSE DESIGN	—	20° TAPERED TIP (FROM CENTERLINE)

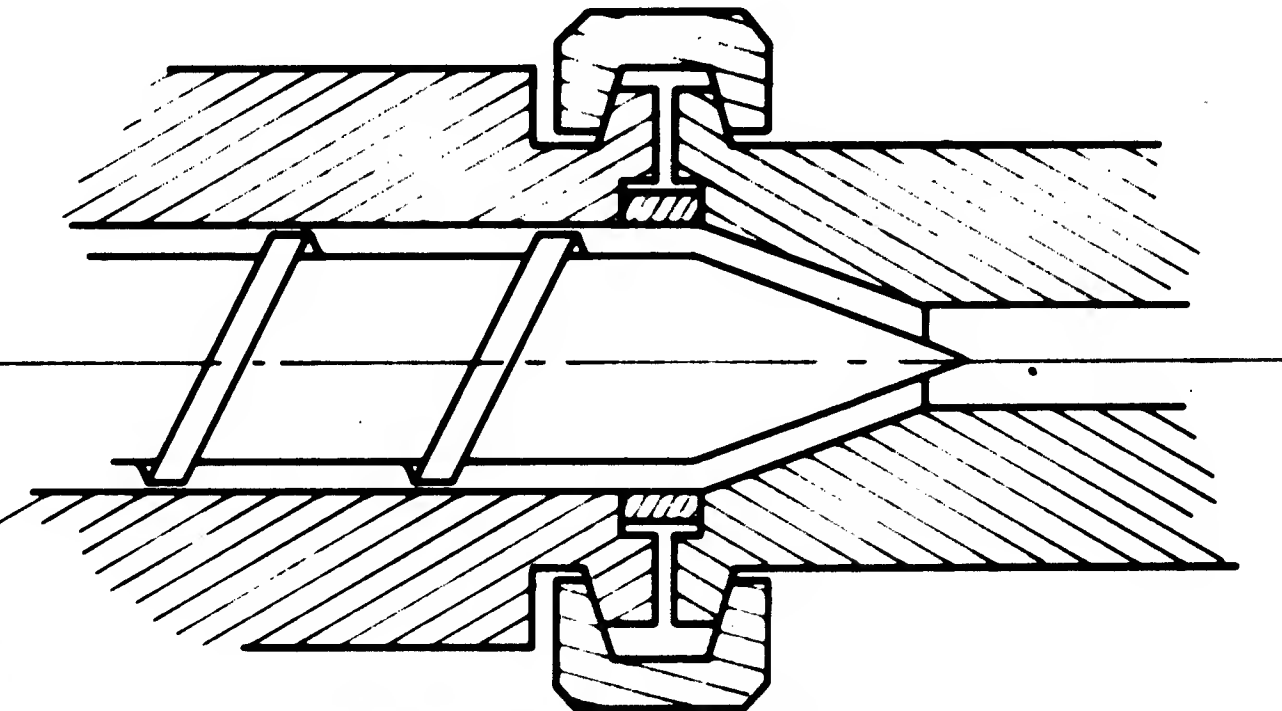
Figure 12.

SCREW NOSE DESIGNS



ORIGINAL DESIGN WITH BREAKER PLATE

Figure 13.



FINAL DESIGN WITHOUT BREAKER PLATE

TYPICAL EXTRUDER CONDITIONS EXPANDED POLYSTYRENE SHEET

Extruder	2½ inches, 24:1
Screw	17 Flight Metering
Die	5 inch Bottom Feed
Die Gap	.020 inches
Sizing Mandrel	13 inches
Feed	Expandable Polystyrene Pellets
Barrel Temp., F.	
Zone 1	220
2	265
3	210
4	200
5	200
Adapter	210
Die Zone 1	220
Zone 2	225
Stock	225
Barrel Pressures, psi	
Zone 1	100
2	500
3	1000
4	1300
5	2200
6	3200
7	2000
Extruder Drive	
Screw, RPM.	40
Amps.	26
Output, lbs. hr.	120
Line Speed, FPM	14.8
Sheet, Thickness	55-62 mils
Density	6.2 pcf
Width	20¼ inches

Figure 14.

TYPICAL PROPERTIES EXPANDED POLYSTYRENE SHEET

Thickness, mils	50
Density, pcf	6.5
Basis Weight, lbs./ 1000 sq. ft.	27
Tensile Strength, psi	400-500
Ultimate Elongation, %	1.8-2.0
Tensile Elastic Modulus, psi	4000-5000
Burst Strength, psi	26
Grease Resistance	
Transudation Time, Sec.	>1,800
Water Absorption, lbs. sq. ft.	0.003
Water Vapor Transmission	
g 24 hrs. 100 sq. in.	
at 73.4°F and 50% RH	0.9
at 95 F and 90% RH	2.9
Cell Size, mils	4-8

Figure 15.



Figure 16.



Figure 17.



Figure 18.

PERCENT EXPANSION VS SHEET AGE

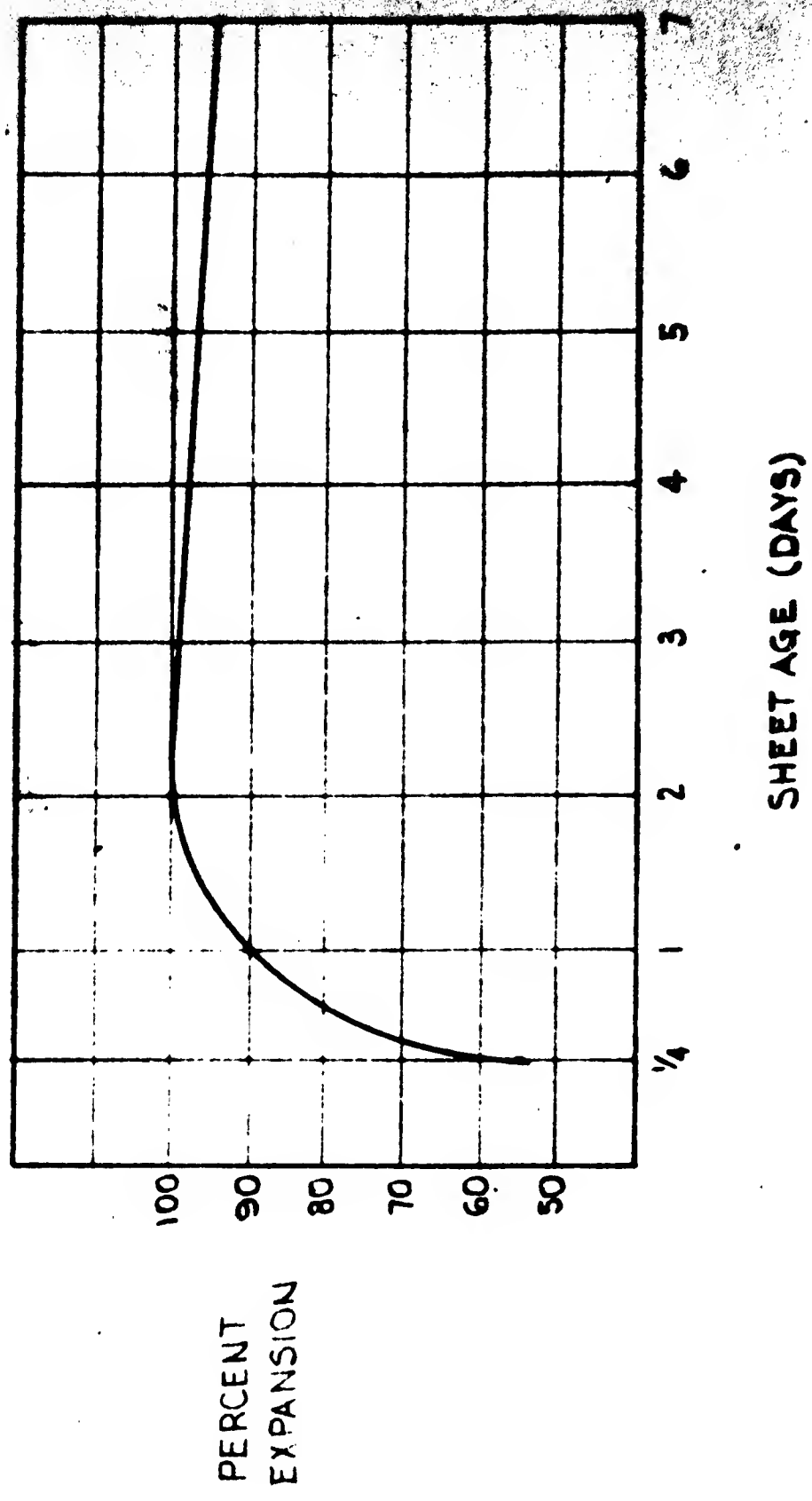
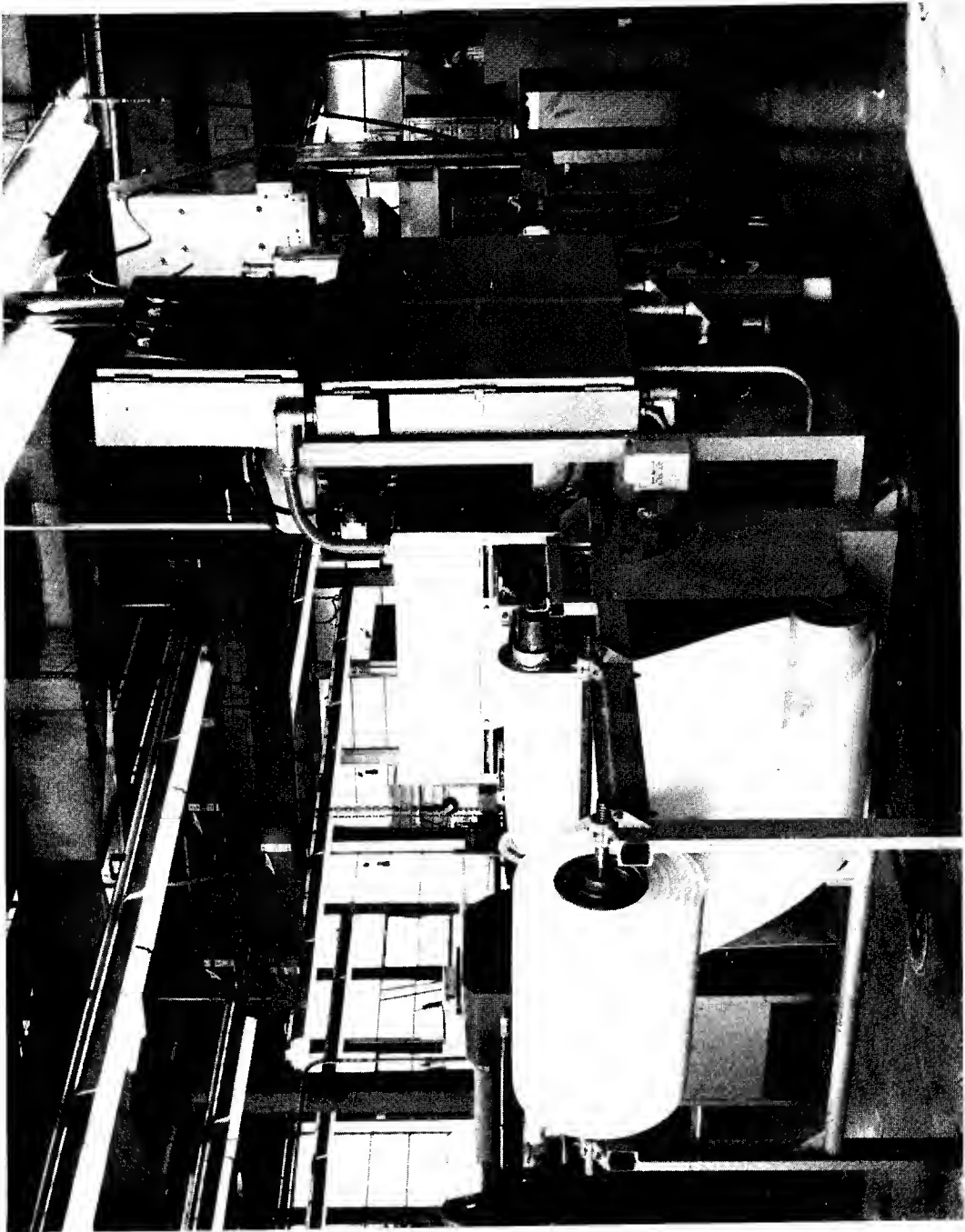


Figure 19.



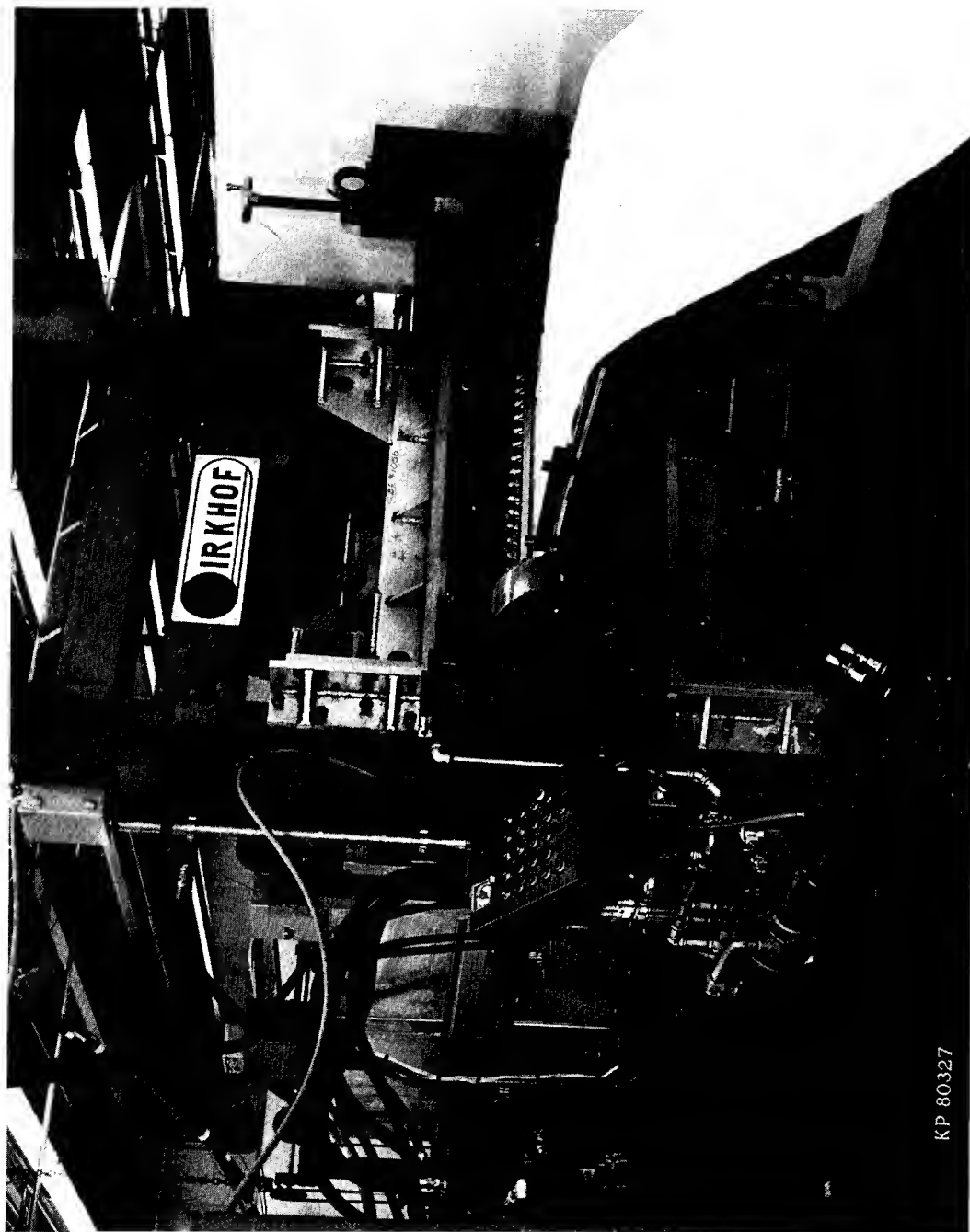
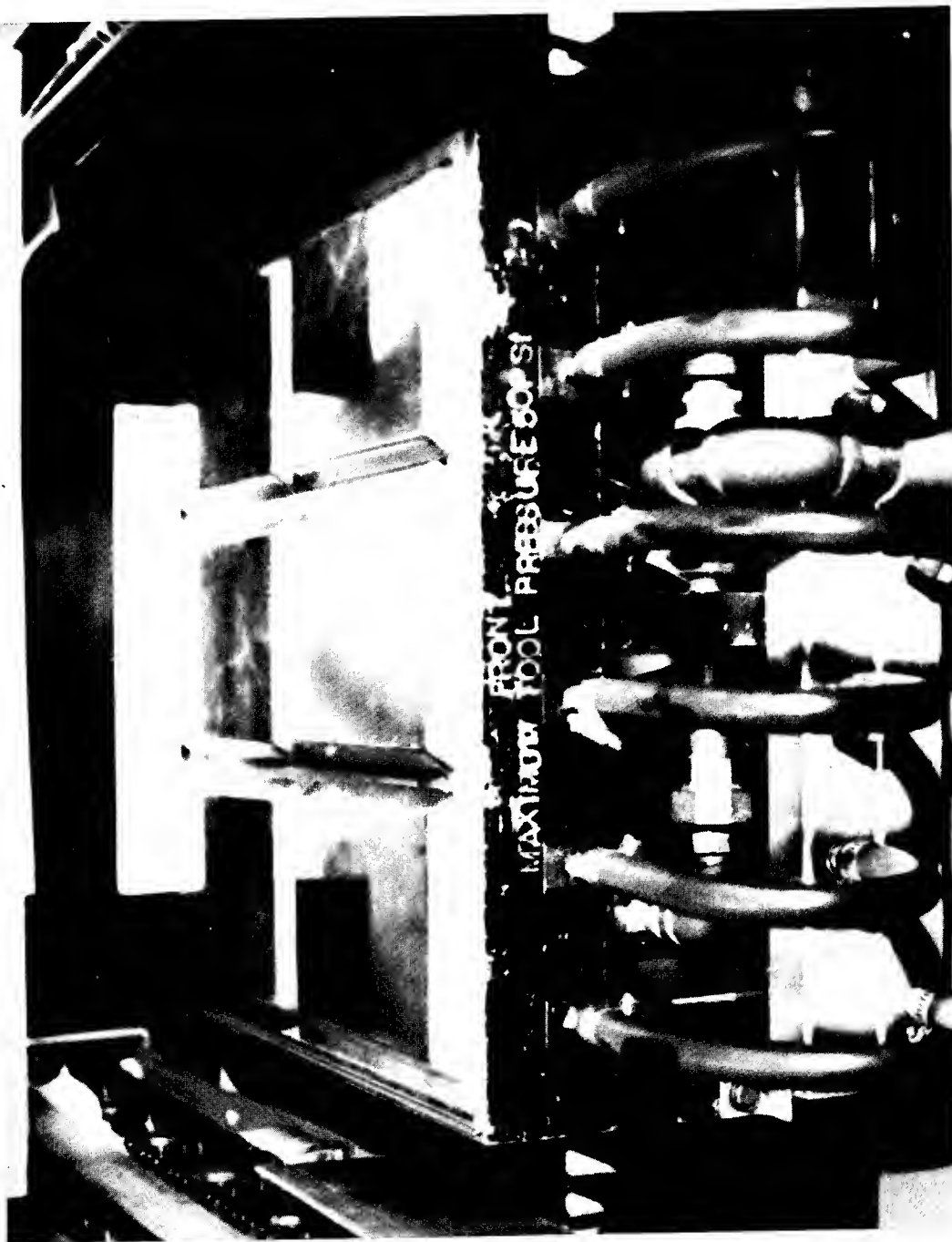


Figure 21.

KP 80327



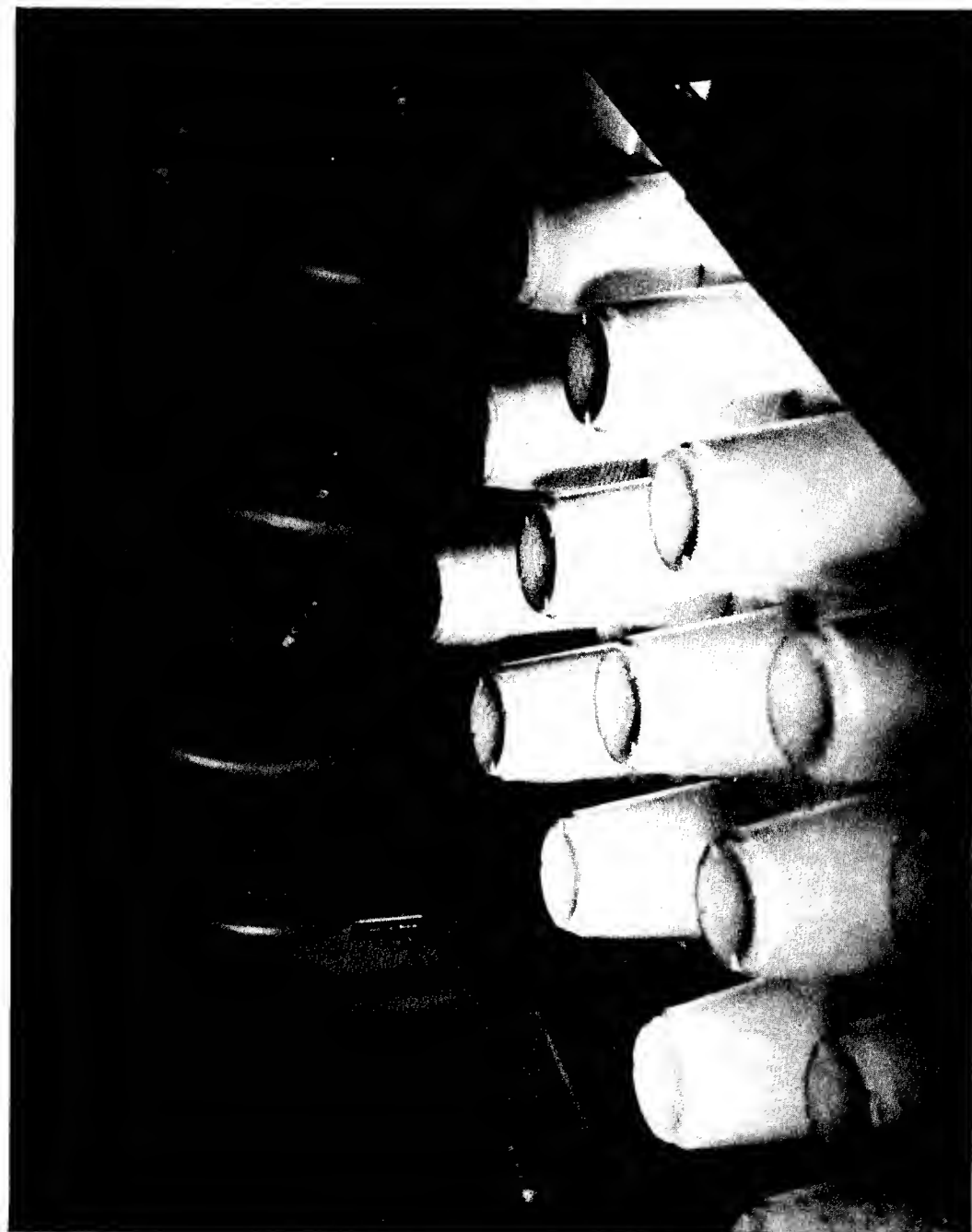


Figure 23.

TYPICAL THERMOFORMING CONDITIONS EXPANDED POLYSTYRENE SHEET

Mold Configuration	
Size, Inches	18 x 18
Number cavities	4
Sheet Characteristics (unformed)	
Thickness, mils	60
Density, pcf	6.5
Width, inches	20
Forming Conditions	
Top Heater, %	24
Top Heater, F	700
Bottom Heater, %	22
Bottom Heater, F	650
Plug Temperature, °F	70
Mold Temperature, F	70
Blow Pressure, PSIG	OFF
Total Cycle, Sec.	3.5
Formed Parts	
Thickness, mils	110-115
Density, pcf	3.2

Figure 24.

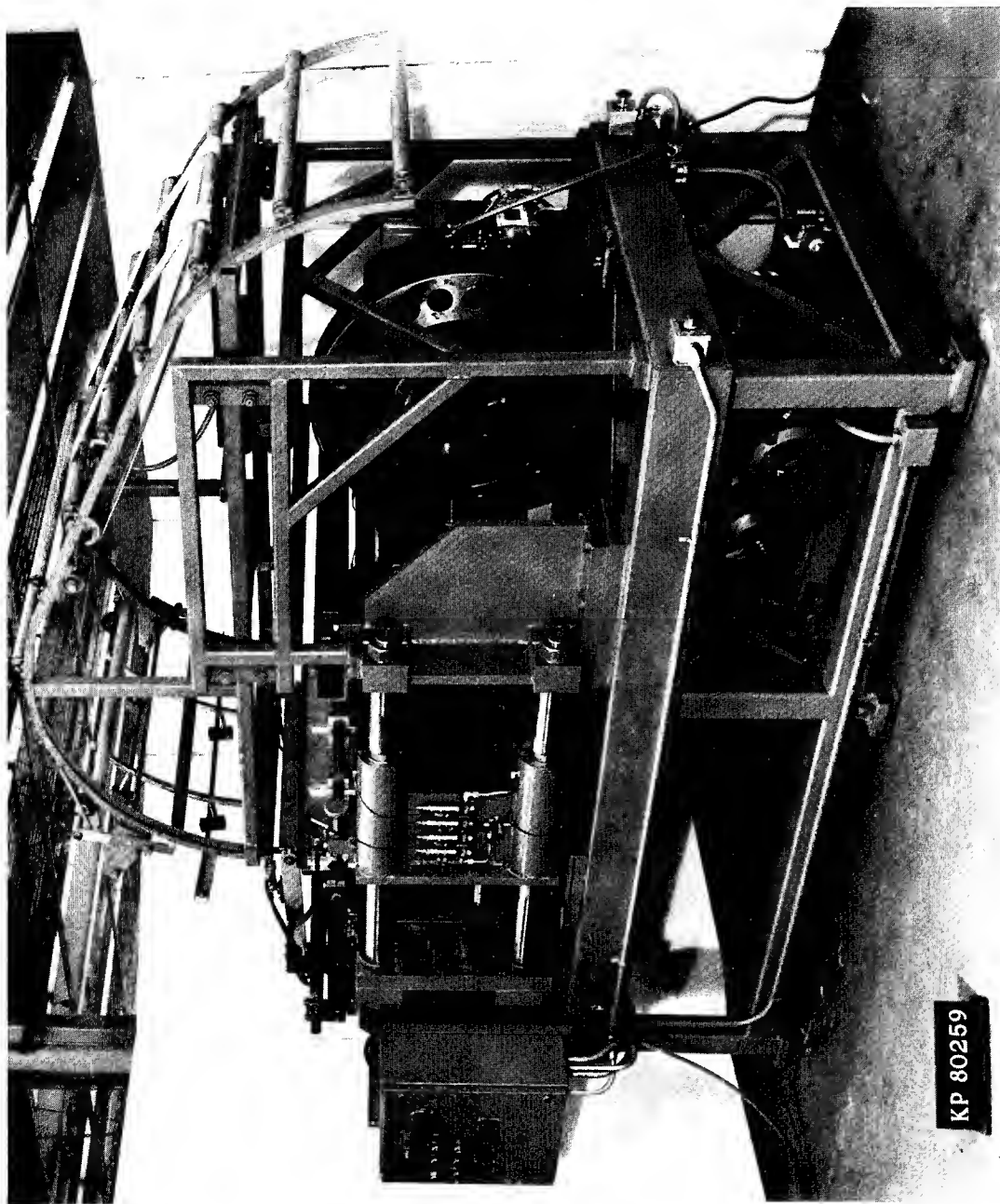


Figure 25.

10214-13

CELLULAR PLASTICS IN PACKAGING APPLICATIONS

511611
R. J. Winne
Westinghouse Electric Corp.

CELLULAR PLASTICS IN PACKAGING APPLICATIONS

I have been asked to cover the application and use of cellular plastics in the area of packaging.

In order to do this, let us review those materials which can be foamed and have been used in packaging. Rubber, epoxy, polyvinyl chloride (plastisols), silicones, phenolic, cellular acetate, urea formaldehyde, polyurethane as well as styrene and its copolymers have been used, some have been found wanting, others have enjoyed a good measure of success.

Rather than delve into a dissertation on the specific properties of each material, I think it will suffice to identify those materials which have commercial importance and only talk about their properties which are important from the packaging standpoint. The most significant are as follows: (Figure 1).

FOAM PROPERTIES IMPORTANT TO PACKAGING APPLICATIONS

- Lightweight
- Cushioning Ability
- Moisture Resistance
- Ease of Fabrication
- Non Dusting
- Chemical Inertness
- Useful Temperature Range
- Thermal Insulation
- Customer Acceptance
- Competitive Cost

Figure 1

The cellular plastics which have best met the test in the market place and are now commercially important are polyvinyl chloride (plastisols), polyethylene, polyurethane, both rigid and flexible and expanded polystyrene. The latter is the industry workhorse.

The following charts Figures 2, 3, illustrate the growth curves of both rigid and flexible urethane and expanded polystyrene in all end products and packaging use.

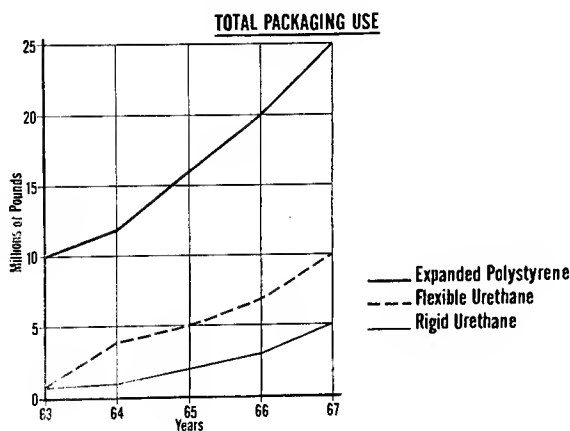


Figure 2

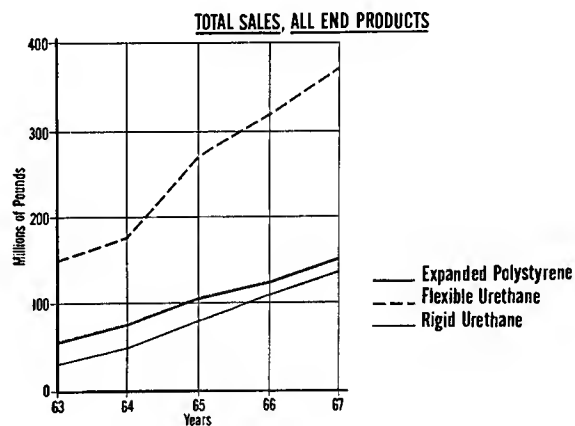


Figure 3

They all indicate good and continued growth with no sign of leveling at this time. Packaging techniques using these materials vary with the choice of properties most desired for a specific application, product volume, value of the product and the ease of fabrication or manufacture.

Specific applications will be covered later.

Next let us review the types of packaging existing today.

Packaging can be broken down into four basic categories.

1. Consumer
2. Industrial
3. Military
4. Export

Simple definitions are as follows:

Consumer Packaging

Packaging which is sales oriented at the retail level.

Graphics, novel shapes tending toward display and convenience for the purchaser are paramount. The selection of the structural material is limited only to the properties of the product itself.

Industrial Packaging

Packaging that is directed toward utility optimizing labor and material costs. It covers the full gamut of industrial products, the non retail items, those which must be contained and protected, during handling, transportation, storage and final use.

Military Packaging

Packaging and preservation of all items procured for use by the military services. Specified by the services and designed generally for long time storage.

Export Packaging

Packaging of consumer or industrial products modified to meet the rigors of export. The most important feature would be protection. Cellular plastics have been used in all categories successfully.

In creating a package we must meet the customer's needs and design the package to fit the sophistication of the distribution system at a balanced cost. The distribution system is and can be a very complicated environment of handling, storage and transportation.

The package, then, can in effect be looked at as the interface between the product and its environment, the product and the ultimate user.

Before we look at specific illustrations of cellular plastics and their applications in packaging, I should like to say that packaging requirements have dictated using the best material for the job available at any given point in time. Historically, glass, metal, forest and animal products and combinations of these materials have found their niche. As new forms of materials developed they were studied for use in packaging. Very few, other than exotic materials, have not been used in some way in packaging. As cellular plastics became available at costs consistent with good packaging practices based on improved technology, their place was assured in the field of packaging. They have generally displaced forest products, however, bonded fibers, springs and shock mounts have also been affected in a lesser degree.

As we develop this paper, please note the classic shapes and techniques for capturing the different geometries of the various products positioned in the packages. These shapes take the form of trays, rails, end bells and corner blocks which also can be used in combination with each other.

Specific Examples of Packaging

Polyvinyl Chloride (Plastisol)

Foamed polyvinyl chloride is presently being used to coat high-volume products which have surfaces needing protection. The material which contains a heat-activated blowing agent is applied to automotive trim (see Figure 4) by a curtain coater (see Figure 5).



Figure 4

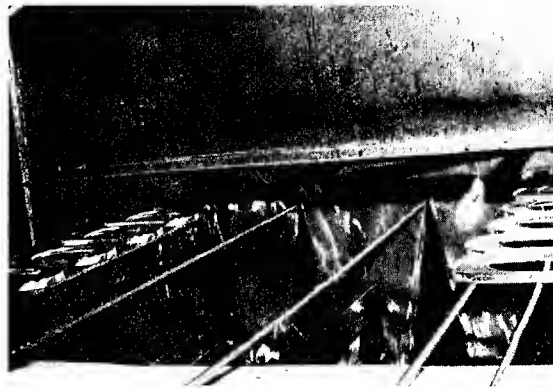


Figure 5



Figure 6

Coated pieces are then conveyed through an oven at 360° (see Figure 6) where the material foams and cures, increasing its thickness about 20 to 30 times. Non-foamed plastisols can also be used depending on the degree of protection required.

This system's basic advantages are as follows:

1. Elimination of inventories on numerous size envelopes, boxes, etc.
2. No setup required to change from one size part to another.
3. Maximum nesting of the packaged parts for storage.
4. Easy removal and disposition of the package by the customer.
5. Ready identification of the product.
6. It is virtually scrapless.

The future of the process is very bright. Presently it is used almost exclusively by the automotive industry.

Polyethylene

Polyethylene, an early comer in foam packaging, captured several special market segments. Because of the shapes available, (slabs, rounds and billets)(see Figure 7), it was easy to fabricate with conventional wood working equipments. It could be easily cut with hot wires or formed using special heated dies. This tough resilient material has been used to block and brace high value, low-volume products in all types of containers. It also found use in packages used to sample pharmaceuticals. Figures 8 and 9 illustrate several techniques used.



Figure 7

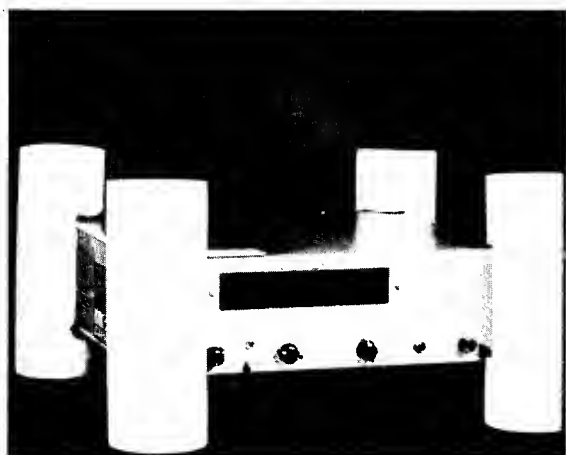


Figure 8

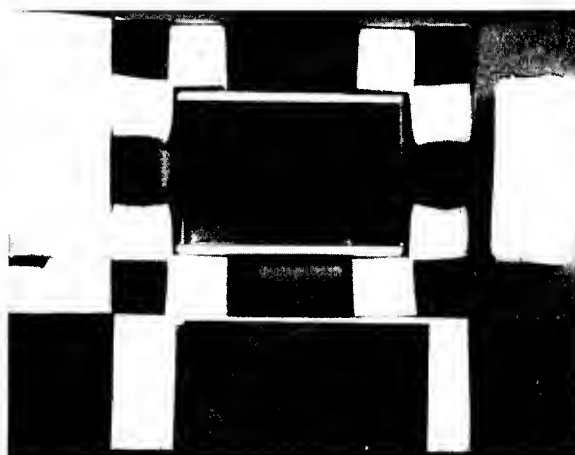


Figure 9

Polyurethane

The next cellular plastic material polyurethane can be either rigid or flexible or some place in between depending on formulation.

The rigid material can be cast in billets, fabricated into slabs, and these in turn worked into packaging components. Cut rigid foam has one

disadvantage. It is friable and tend to be abrasive, otherwise its ratio of weight to strength is excellent.

Foam-in-place packaging had a magic appeal for both packaging people and resin manufacturers. The technique seemed so simple. The thought that you could mix two prepared components, pour them around a part in a container and foam-in-place would occur. Unfortunately, it wasn't that easy. Problems of equipment, formulation, technique, and costs contributed to this process's slow growth.

Airplane engines, typewriters, high value electronic gear have been packaged using this technique. Usually the part is placed in a film bag, suspended or prepositioned on foam pieces then the liquid resin is poured in foaming around the part when required. Rip cords are inserted prior to the foaming for product decasing. Figure 10 illustrates an engine package.

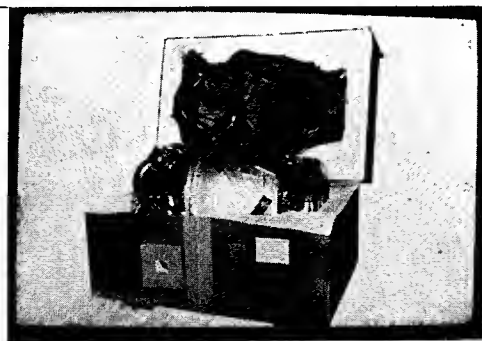


Figure 10

Another technique is to place the premeasured liquid mix in a film bag placing the bag as the resin foams in a critical position on the part being packaged. Figure 11 illustrates this technique.

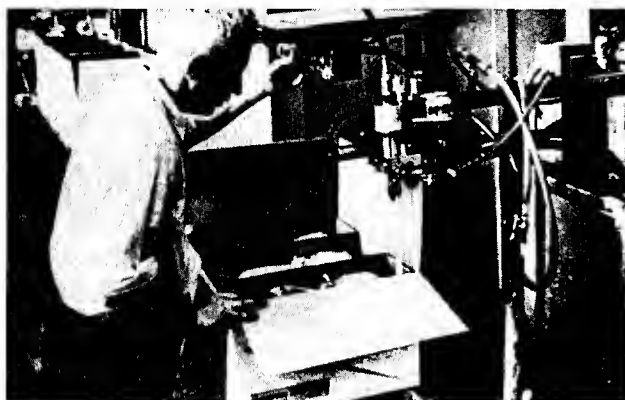


Figure 11



Figure 12

Spraying the resin in containers around or on products has also recently been demonstrated. Pleasure boats with a sprayed-on cover over the cockpit protects boats against damage and exposure during handling and storage. See Figure 12.

Rigid urethane, because of many good qualities, but especially the K factor, has been used in the construction of the frozen food containers. Although the term containerization has been coined to describe this type unit it is still just a large package. Figure 13, 14 illustrate these units.

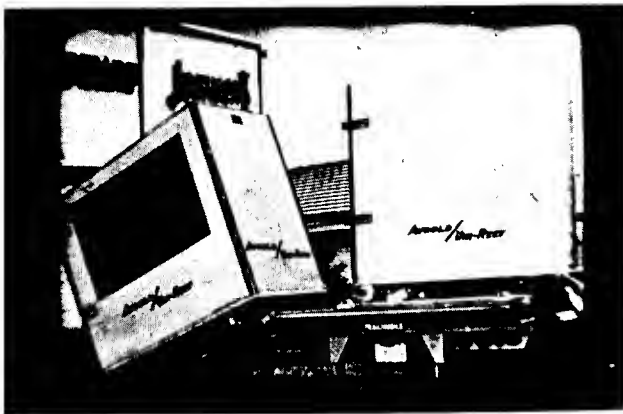


Figure 13

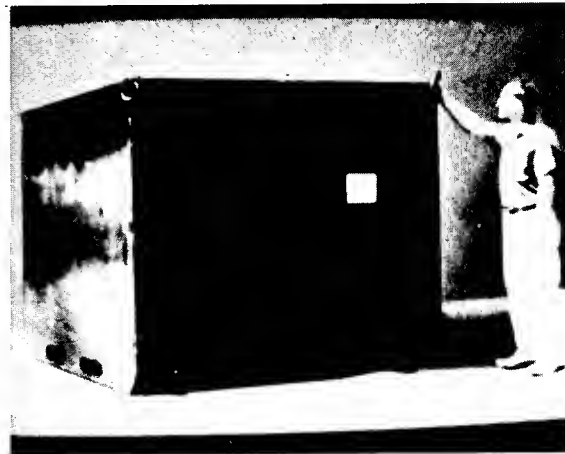


Figure 14

Flexible polyurethane material has contributed much to packaging. It may be fabricated by contour cutting, molded -- sheets may be used as wrappers and several proprietary devices have been developed. Bonded shredded scrap has also been used successfully.

Figure 15 shows a form of urethane foam fabricated by contour cutting. The product is space hardware in a carrying case. The insert contour is cut to the shape of the unit and it's accessories.

The foam in this unit is 2 lb. cu.ft. density meeting specification MIL-P-26514.

The package, see Figure 16, was tested to the cycling and resonant conditions of procedure VI, Specification MIL-E-4970 USAF. The package was also drop tested from 30" on two edges, two opposite corners

and all six faces of the package. It passed and was air-tight after the test. Testing is a very important part of packaging.

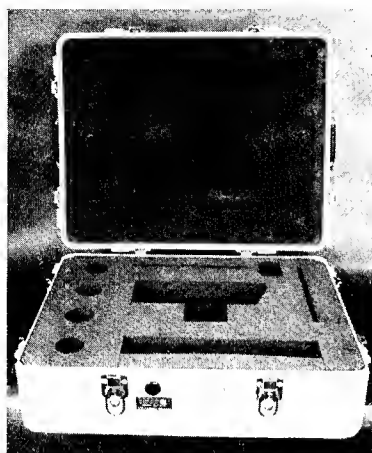


Figure 15

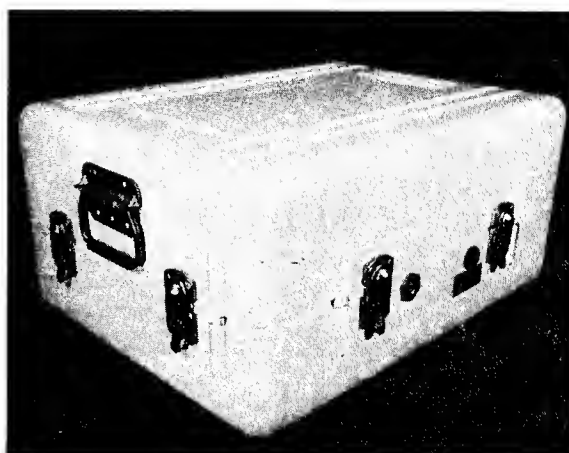


Figure 16

Molded flexible urethane has had a degree of success in the packaging field. Its ability to cushion and maintain low "G" factors has been the main reason for this acceptance. Figure 17 illustrates the cushioning factors of the various foams.

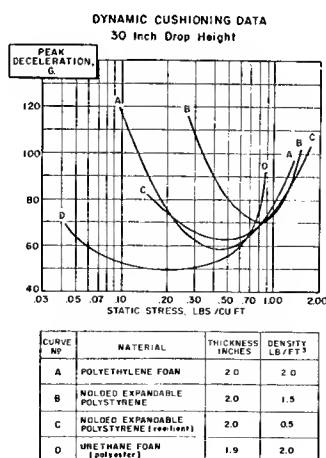


Figure 17

An example of molded flexible polyurethane is illustrated in Figure 18. Many proprietary devices have been developed. Figure 19 illustrates the use of a flexible urethane which has been manufactured and is used as a corner block device, one which can capture a box-in-box situation, cushioning the inner box sufficiently for the needs of the product. Figure 20 shows a contour cut propriety unit.

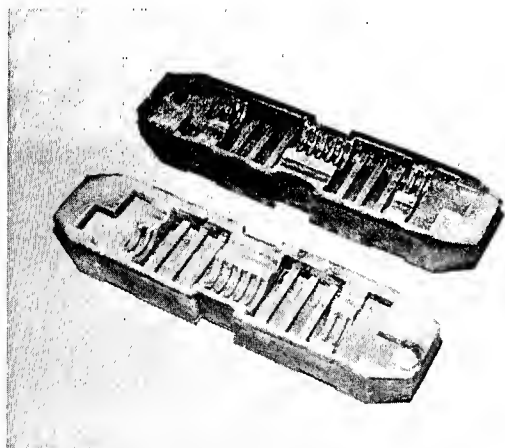


Figure 18

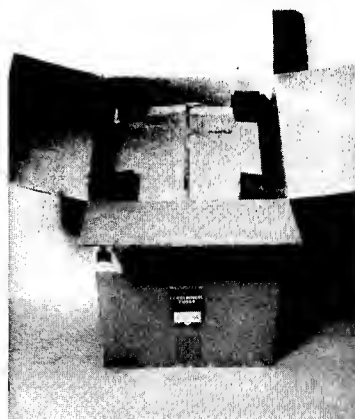


Figure 19

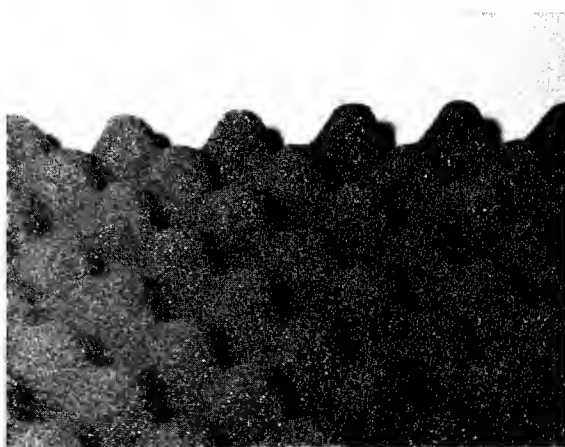


Figure 20

Recently, I saw a molded unit approximately 2" thick, 6" to 8" in diameter molded to plywood caps. This could be used as an isolation mount for skidding large fragile items.

I should also like to point out that flexible urethane (sheets) used as a wrapping material has been in many instances very grossly used. Indiscriminate use by those who feel it is a panacea are at fault. It can be expensive if improperly applied.

Polystyrene

As stated before, polystyrene in its various forms has been the workhorse of the cellular plastic packaging materials. The available forms used for packaging are: (1) parts and components fabricated from bead board and expanded polystyrene, (2) parts and components molded from beads, (3) parts and components pressure formed from expanded extruded sheet (this sheet can also be used as a wrapper), (4) loose fill material which is available in several forms. The most important one being extruded strands which can be expanded. Chopped, slit or ground scrap may also be used in this method.

Recently, a device was announced which coats expanded beads with a cohesive material, allowing the beads to be virtually poured and shaped around a packaged part in a container.

Fabricated packaging components made from slabs and blocks of EPS was the first method used. This material can be easily worked with conventional woodworking equipment and hot wire cutting devices.

This, incidentally, is the way that the majority of prototype samples which are to be molded are constructed today. This method has its advantages in that samples can be made from a known density material, fabricated, weighed and a very accurate material cost determined. Because of the peculiar geometry of some devices, this is the simplest way to get the right answer.

Since the basic difference between the use of fabricated and molded pieces is volume and the classic shapes of trays, end bells, corner or end pads have evolved, the following examples could be manufactured either way.

It has been possible in many instances to begin using fabricated pieces for start up of low volume items. As demand increases the volume, it very often becomes necessary to utilize the economics of molded units previously fabricated. This transition is illustrated in Figure 21. The product which is packaged in these trays is a solid state device used in automobile alternators. The white tray on the left was fabricated by heat deformation. As the business increased sufficiently, the trays were molded more economically than they could have been fabricated. They are color

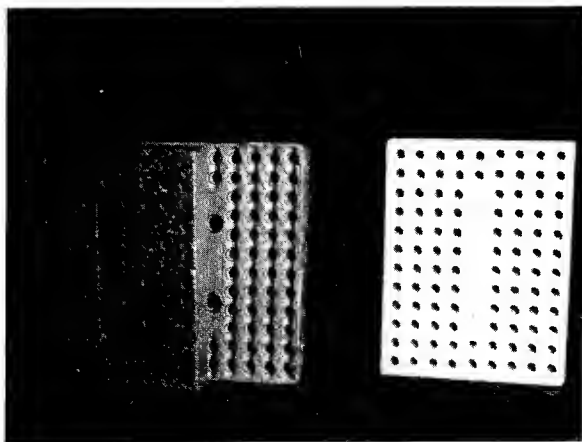


Figure 21



Figure 22

coded to indicate polarity. The first Westinghouse use of molded EPS was in 1959. A breaker switch which had been packaged in a conventional corrugated rat traps (see Figure 22) was changed to molded end bells (see Figure 23). We combined EPS and shrink film in one of the first combinations. (see Figure 24). The product was a small portable mixer. We used a colored tray of EPS. Another shrink film EPS combination is the stereo cartridge shown in Figure 25.

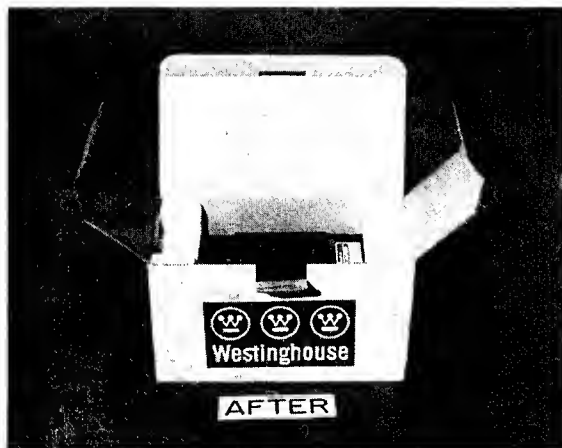


Figure 23

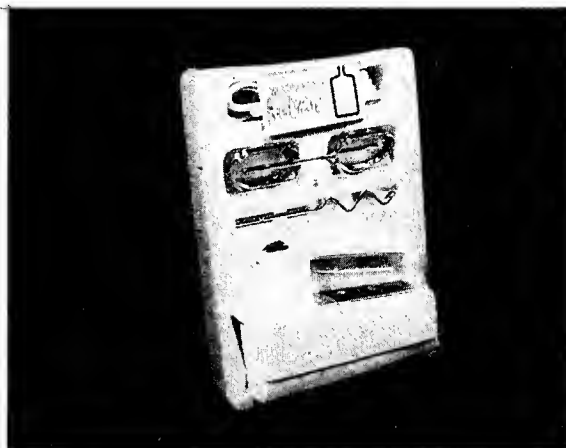


Figure 24

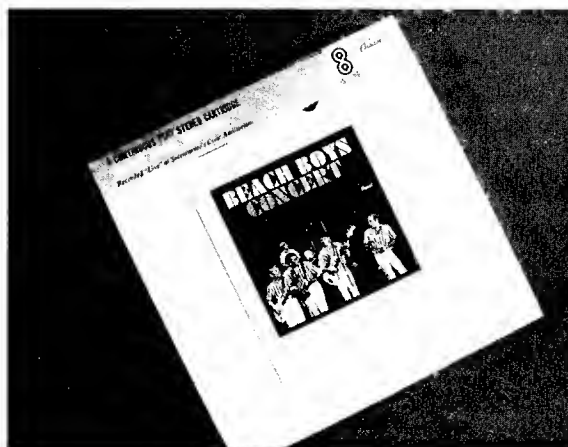


Figure 25

Total encapsulation, a shipping container, is illustrated in Figure 26. This container would be closed by banding or taping.

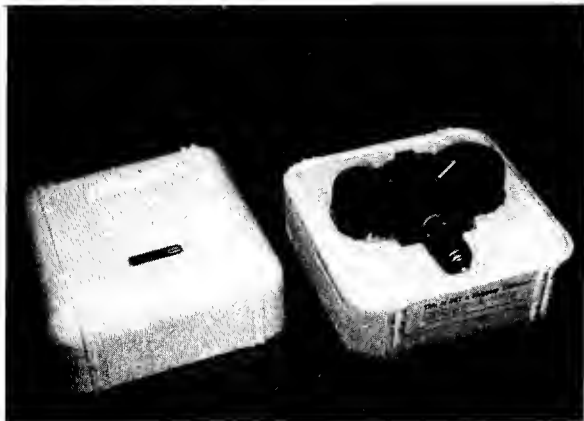


Figure 26



Figure 27

Next, let us look at combinations of material where the best properties of each packaging material are used advantageously.

The standard tube and cap container (see Figure 27) utilized corner posts in refrigeration packaging for years.(see Figure 28) Top pads were developed and after much testing were adapted.(see Figure 29). There was a substantial cost reduction in both labor and materials as a result of this change.



Figure 28



Figure 29

Foam end caps and a corrugated tube, replaced a 5-panel folder -2 corner cut inserts and 2 pieces of wadding formerly used to package this wallboard heating unit. See Figures 30, 31, which show the molded ends the unit which was taped for closure. Better stacking and protection resulted from this development.

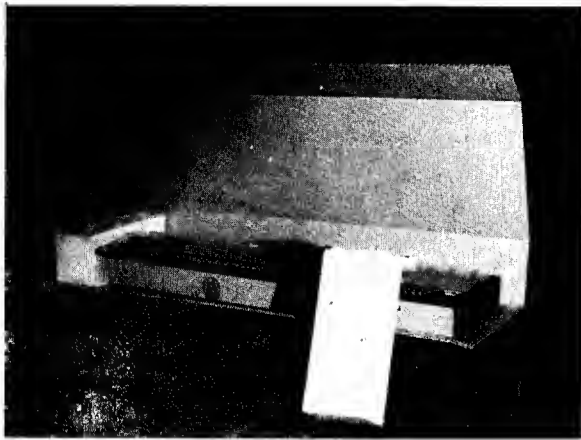


Figure 30



Figure 31

Figure 32 shows a special electronic tube package developed for shipping and storage. The shipping container is corrugated the "top hat" molded urethane end components, positions and cushions the expanded polystyrene molded case. The EPS case can be used as a storage unit on shipboard, discarding the other packaging material.

The potential of expanded extruded sheet is just now beginning to emerge. High volume application such as for produce and meat trays, which are pressure formed are gaining acceptance in the market place.



Figure 32



Figure 33

The last method of packaging using polystyrene is loose fill material made from extruded strands which can be expanded for use as shown in Figure 33. This is a shipping room product used mostly for non-standard, low volume, fragile items.

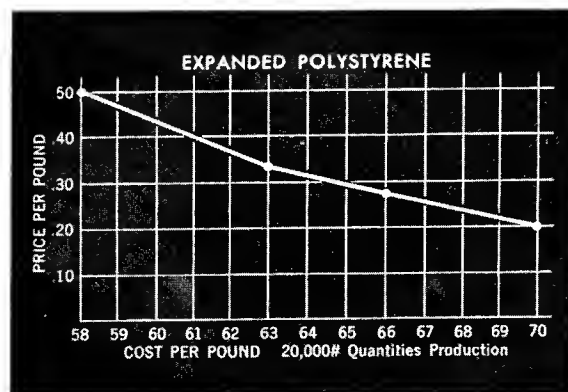


Figure 34

The preceding foam packaging applications have demonstrated how foam, if properly applied, can be used to fit both the needs of the customer and the needs of the distribution systems. In all cases the packaging costs were reduced. Package performance has almost always improved with the use of foam and the use of it carries the connotation of quality. These factors along with the cost trend have contributed to the continued growth of cellular plastic in the area of packaging. The polystyrene bead cost trend shown in Figure 34 illustrates the latter point.

The package designers will continue to increase their use on both existing and new products. These materials are still in their infancy and I predict will continue to grow at their present prodigious rate.

10214-14

CHEMICAL AND MECHANICAL FACTORS AFFECTING

ONE-SHOT RIGID URETHANE FOAM

by

M. Kaplan

INDUSTRIAL CHEMICALS DIVISION
ALLIED CHEMICAL CORPORATION
BUFFALO, NEW YORK

Formulating and processing rigid urethane foam are both a science and an art. It is a science in respect to the theoretical aspects concerning the catalysis and kinetics of the polymerization and crosslink density of the resulting foam. It should, however, be considered an art since trace impurities or only minimal changes in formulation or mechanical processing can result in a foam with a radically different appearance and/or physical properties.

INTRODUCTION

Rigid urethane foam is recognized as an outstanding material for insulation applications. It has many desirable properties such as:

- (1) low thermal conductivity
- (2) low density
- (3) excellent dimensional stability
- (4) high strength-to-weight ratio
- (5) low moisture permeability
- (6) low water absorption

which make it particularly suitable for application in household refrigerators⁽¹⁾⁽²⁾, refrigerated trailers⁽³⁾⁽⁴⁾ and railroad cars, construction and industrial insulation.

The rapid acceptance of rigid urethane foam can be attributed to the commercialization of the more economical one-shot method of foaming. Prior to this, all foaming was accomplished by the quasi-prepolymer method, which consisted of blending a premix containing 80-90% of the polyol and all other formulation

ingredients with a quasi-prepolymer. The quasi-prepolymer was made by pre-reacting all of the diisocyanate with the remaining polyol. The one-shot method involves only the blending of the premix with the diisocyanate immediately before foaming. Thus, significant saving is accomplished by reducing the manufacture of foam from a two-step (quasi-prepolymer preparation and foaming) to a one-step (foaming) operation. The use of a modified tolylene diisocyanate(*) offers a more controlled reaction than with distilled TDI; as well as, improved physical properties and economics (5)(6)(7). In addition, the one-shot system based on modified TDI with a lower viscosity has improved mixability and flow of the liquid mix before and during foaming. This characteristic is particularly desirable for filling complex molds (pour-in-place application). The higher equivalent weight of the modified tolylene diisocyanate produces rigid foams with lower maximum exotherms and subsequent elimination of burnout in slabstock applications.

There are three general methods of rigid urethane foam application:

1. Poured-in-Place⁽⁸⁾ - (accomplished by conventional or froth foaming technique) - used for filling irregular voids with foam.
2. Slabstock⁽⁹⁾ - used in applications where foam can be most economically cut to required shapes.
3. Sprayed⁽¹⁰⁾ - used in applications where field moldability is required.

This paper discusses the chemical and mechanical variables which affect the rigid urethane foam produced by the pour-in-place or slabstock techniques.

*NACCONATE[®] 4040 - Allied Chemical Corporation

The contribution of each formulation ingredient to the properties of the finished foam is chemical in nature, whereas, metering and mixing of the ingredients, mold or conveyor design and automation of the foaming operation are distinctly mechanical.

Early one-shot pour-in-place foam formulations produced good moldings having low thermal conductivity and excellent dimensional stability. However, improvements in several properties were desired. These included the attainment of reduced shear (non-uniformity) of the panel surfaces, reduced panel density with little or no change in properties, and improved adhesion of the foam to the substrate. Several experimental studies involving numerous formulation and processing variables resulted in the solution of these problems through slower foam gelation, optimum mold temperatures, and surface treatment of the substrate materials.

A typical molding formulation and important processing variables are shown in Table I. Typical physical properties of a foam panel are given in Table 2.

Early one-shot slabstock formulations possessed inherent disadvantages that restricted attainment of maximum foam yield and uniformity of product. Improvements were desired to eliminate:

1. appearance of burnout in continuous high rise buns
2. non-uniform foam properties throughout buns
3. tendency toward external splitting
4. rapid foam gelation which prevented the molding of buns with rectangular cross-section

A formulation and processing condition for production of one-shot rigid slabstock without these disadvantages is shown in Table III. Typical physical properties of the foam are given in Table IV.

CHEMICAL FACTORS - POURED-IN-PLACE AND SLABSTOCK

Polyethers

Rigid foam polyethers are usually based on sorbitol, sucrose, pentaerythritol, methyl glucoside or similar polyols. In general, foam physical properties, especially dimensional stability, improve with increased polyether functionality and hydroxyl number. High functionality is helpful in attaining the highly crosslinked rigid polymer that is necessary for good dimensional stability in the finished foam.

The hydroxyl number of the polyether (a measure of equivalent weight of the polyether) usually falls within the range of 300 to 550 units. High hydroxyl number polyethers (e.g., 450 to 550) generally produce one-shot rigid foams having good dimensional stability. However, as the hydroxyl number increases, the foams have a tendency toward friability. Since friability (foam brittleness) has an adverse effect on foam strength, a compromise must be made. The best balance of properties of one-shot foam has been attained in a hydroxyl number range of 430 to 530, (Figure 1) the exact hydroxyl number depending on the specific polyether type. Conversely, low hydroxyl number polyethers (300 to 400) usually produce soft, non-friable foams having correspondingly poorer dimensional stability.

Small amounts of water in the polyether generally result in slight increase in "K" factor and friability of the foam. Improvement in dimensional stability is normally observed.

The phosphorus containing polyether in the formulation of Table III inhibits the development of burnout in continuous high rise buns*. Although the mechanism of burnout is not fully understood at this time, the addition of small amounts satisfactorily controls the polymer degradation process. Other materials, such as resorcinol, substituted phenols, and organic phosphates and phosphites, in small amounts, have exhibited a similar effect.

Polyisocyanate

The polyisocyanate used in one-shot formulations described here is a modified toluene diisocyanate. Its relatively high acidity (0.2%) gives it a reduced degree of reactivity which permits slow gelation and rise times, both of which are helpful in panel and slabstock moldability.

A TDI Index (ratio of NCO/total active H) of 1.03 to 1.05 produces optimum results. Lower isocyanate levels can result in poor dimensional stability and cell wall rupture at elevated temperatures resulting in an increase in thermal conductivity. Higher levels do improve dimensional stability, but density and friability is generally increased.

Silicone Surfactant

The silicone surfactant serves a dual function. First, it serves to emulsify the hydrophilic polyether and the hydrophobic isocyanate and fluorocarbon into a homogeneous mixture, thus

*Patent pending

insuring uniform reaction throughout the foam mass. Second, it controls cell size by stabilizing the rising foam and preventing coalescence of the tiny foam cells until gelation occurs.

Catalysts

The most critical formulation ingredients in rigid foam production are the catalysts, which control the rate of polymerization and rise of the foam.

The preferred catalysts and their contributions to one-shot foaming are:

Triethylenediamine: This catalyst gives the rapid initial polymerization that is essential for fine uniform cell structure, yet gelation or hardening of the foam is delayed until rise is almost complete.

N,N-Dimethylethanolamine: This catalyst serves to neutralize the acidity in NACCONATE 4040, thereby increasing the basicity of the system and controlling the rate of polymerization. Excessive amounts tend to reduce foaming times slightly but have little effect on moldability.

N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine: This catalyst improves moldability of the system and functions as a crosslinking agent to improve dimensional stability.

Dibutyltin dilaurate: This catalyst produces fine cell structure and promotes rapid gelation or hardening of the foam. Concentrations above 0.03 parts by weight/100 parts polyether result in increasing shear and decreasing adhesion.

Stannous Octoate: In the case of slabstock production this catalyst gives the rapid initial polymerization that is essential for fine uniform cell structure, yet final gelation or hardening of the foam is delayed until rise is almost complete. In combination with triethylenediamine, a synergistic behavior is noted which promotes reactivity faster than either catalyst alone.

The optimum combination of catalyst type and concentration is required to obtain the molding characteristics necessary for filling a complex mold. To insure complete mold fill, low shear and good adhesion, gelation should be retarded until the foam has nearly completed rising.

The correct balance of catalysts in maintaining foam moldability in slabstock manufacture is also critical in achieving a bun with a rectangular cross-section (to minimize scrap loss). In addition, external splitting of a bun can occur when an imbalance of catalyst causes premature foam gelation (before complete foam expansion has occurred).

A useful tool developed primarily for studying effect of catalyst variation on foam formulation is the "Rate of Rise Test"⁽¹¹⁾.

Fluorocarbon Blowing Agent

The fluorocarbon serves two important functions in rigid foams. First, it serves as a blowing agent for expansion of the urethane polymer controlling foam density. Second, the fluorocarbon gas, usually trichlorofluoromethane trapped in the foam cells contributes to the low thermal conductivity of the foam because the thermal conductivity of the fluorocarbon itself is extremely low. The initial thermal conductivity is also dependent upon the open cell content of the foam, cell size of the foam, mean temperature, foam density and cell orientation⁽¹²⁾. While the initial K factor of fluorocarbon blown rigid urethane foam is of the order of $0.11 - 0.12 \text{ BTU}/(\text{hr.})(\text{ft.}^2)(^\circ\text{F}/\text{in.})$ at a mean temperature of 75°F , a slight upward drift due to the inward diffusion of atmospheric gas has been observed after extended aging of cut urethane foam samples. As equilibrium is attained, the K factor is in the range of 0.15 to 0.17. However, when foam is enclosed between steel plates, as in a refrigerator wall, this K factor drift is not observed, and the K factor remains at the low initial level.

Initial Temperatures

The temperature of ingredients can play an important part in obtaining proper foam reactivity. In general, reaction rate increases with increasing ingredient temperatures. The effect of ingredient temperatures on reaction times for a pour-in-place system is shown in Table V. At equivalent levels of halocarbon, significantly lower density foams are obtained with hot foam

ingredients than from cooler foam ingredients. (Table VI).

Usually, too short a cream time is undesirable in molding because it may result in poor foam distribution or knit lines and air voids in the molded part. Surprisingly, however, the short cream time attendant to hot ingredients has not caused processing problems. In this case, the foam mix can be poured on top of rising foam without deleterious effect. In fact, shear is actually decreased when hot ingredients are used. Perhaps this difference occurs because short cream time resulting from hot ingredients is not necessarily accompanied by rapid gelation, whereas short cream time caused by too active catalysts is accompanied by rapid gelation; it is the rapid gelation that causes poor moldability.

MECHANICAL FACTORS - POURED-IN-PLACE AND SLABSTOCK

Metering Equipment⁽¹³⁾

In producing one-shot rigid urethane foam, the function of the mixing and metering equipment is to deliver two or more components (streams) to the mixing head in correct proportions and at controlled temperatures.

Mixing Head (Agitator Design)

The function of the mixing head is to provide sufficient mixing so that the streams are thoroughly blended, and the resultant foam has fine, uniform cell structure and optimum physical properties. Insufficient mixing will result in weak foam with coarse, irregular cell structure. The degree of mixing achieved in the head is largely dependent upon agitator design, clearance between the housing and agitator, the size of the outlet

orifice, and agitator speed.

Several agitator designs are useful. (See Figure 2). At equal operating speeds, the pin-type and helical-gear agitator will provide low and high rates of mixing shear, respectively. The high-shear, helical-gear type agitator is preferred because it consistently provides thorough mixing and fine cell structure foam.

The clearance between the housing and the agitator, particularly with the helical-gear type agitator, is very important. A clearance of 0.006"-0.030" between the housing and the helical-gear type agitator provides a high degree of mixing shear and has been found to produce fine, uniform cell structure foam. Figure 3 illustrates a typical mixing chamber. The specific clearance to be used for a particular system depends on ingredient viscosities. Generally, higher viscosities require increased clearance.

Outlet Diameter

Restriction at the outlet of the mixing head creates back pressure and increases the mixing action. The back pressure is also a function of the throughput rate and, therefore, selection of the orifice size must take this into account. Excessive restriction of the orifice tends to result in foam of increased cell size, which is undesirable. Optimum results have been achieved using the smallest orifice that does not significantly increase cell size.

Agitator Speed

Agitator speed may be increased or decreased to bring

about a corresponding change in the degree of mixing. Normal speeds for the helical-gear type agitator are 4000-6000 RPM.

Nitrogen Injection

Injection of nitrogen or dry air into the mixing chamber is recommended. This will provide additional nucleating sites which generally improves cell structure. At 100-150 lbs. per minute throughput rate, nitrogen or dry air injection rates of 0.25-1.0 standard cubic feet per hour produce optimum results. At lower foam delivery capacity, a corresponding reduction in nitrogen or air injection should be used.

Distance of Outlet Orifice to Mold or Conveyor

In the case of slabstock production, smooth laydown of the foaming mix with a minimum splashing is achieved by positioning the outlet close (approx. 2") to the conveyor bottom. If the mix is not deposited smoothly, striations may be present in the foam. If splashing occurs with resultant air entrapment, bubbles or elongated holes may occur. Both conditions have deleterious effects on foam properties.

With pour-in-place panels the distance of the outlet orifice to the bottom of a high rise molded part is not critical.

Traverse Speed

In the case of slabstock production, smooth laydown of the foaming mix is also dependent on traverse speed. Traverse speed must be uniform and equal in both directions and sufficiently fast so that each succeeding deposit of mix immediately flows into the preceding deposit to form a continuous flow of mix. Too fast

a traverse or conveyor speed may cause splashing or uneven distribution of foam mix on the conveyor. With a three foot wide traverse, speeds in the range of 32-40 strokes per minute, at a conveyor speed of nine feet per minute, have provided smoothest laydown.

FOAMING CONVEYOR AND OPERATION OF SLABSTOCK EQUIPMENT

Conveyor Design

The function of the conveyor is to provide a cavity in which the rising foam can be continuously foamed into a bun with the desired shape and dimensions. Generally, a conveyor with four synchronized drive belts on the bottom, sides and top is utilized. Steel slat-type conveyors or canvas belt conveyors supported by steel plate are normally used.

Tilt

The conveyor must be tilted downward away from the mixing head so that the foam mix flows away from the mixing head immediately after being deposited on the conveyor bottom. This prevents succeeding layers of foam mix being poured on top of previous layers as the head traverses and avoids defects (splits, knit lines, etc.) in the bun. A tilt range of 6 to 10 degrees is satisfactory for rigid slab operations.

Release Paper and Feed

Continuous rolls of release paper are fed onto the moving conveyors to prevent the foaming mass from contacting the conveyor surfaces.

Storage

The slabstock buns must be cured for 16-24 hours, to allow development of optimum properties and release of exothermic heat of reaction prior to further processing. The buns should be stacked with sufficient separation for cooling in a room which is adequately ventilated to remove the heat.

Conveyor Speed vs. Throughput Rate, lbs./min.

To achieve maximum yield, a bun with a rectangular cross-section is required. For a given conveyor opening and foam density, the conveyor speed is directly proportional to the throughput rate and expressed by the following relationship:

$$\text{Conveyor Speed, ft./min.} = \frac{\text{Throughput, lb./min.}}{\text{Density, lbs./cu. ft.} \times \text{width, ft.} \times \text{height, ft.}}$$

Cream Time

The primary performance indicator in continuous slabstock manufacture is the nature of the cream line. The cream line is that area on the bottom conveyor where the liquid mix flowing down the conveyor shows cell formation and initiation of rise. It is observed by a lightening (or creaming) of the liquid mix. Satisfactory operation is evidenced by a cream line which shows "fingers" or "streamers" from 3" to 12" in length. If the liquid mix "undercuts", or flows beneath the rising foam, the "fingers" are not apparent and the foam bun will usually show splitting. Splitting causes considerable yield losses in fabrication. Undercutting usually occurs when the initial reaction

rate is too fast and creaming occurs too close to the mixing head. The position and nature of the cream line can generally be controlled by varying the level of stannous octoate catalyst in the formulation, the conveyor tilt and/or stream temperatures.

MOLD CONSTRUCTION AND OPERATION OF POUR-IN-PLACE EQUIPMENT

Mold Construction

Mold construction is often dictated by the application involved. However, the design of any rigid foam mold cavity must concern itself with materials of construction, adequate jiggling for mold support and venting for release of entrapped gases.

Materials of Construction

Plain and galvanized steel, aluminum and wood are commonly used mold surface materials. Adhesion of the foam to the mold surface is usually an important consideration. Where strong adhesion is desired, the minimum requirement is that the foam-to-mold surface bond strength should equal that of the foam itself. Surface treatment may be required to achieve optimum foam-to-metal bond. Untreated surfaces ranked in order of decreasing bond strength are: wood, steel, embossed aluminum, mill finished aluminum and galvanized steel. Surface treatments for metal molds which improve bond strength include:

1. Chemical etching, such as with phosphoric acid or chromic acid.
2. Application of a primer. (Metalast Washcoat Primer No. 920, C. A. Woolsey Paint & Color Co., Inc., N. Y.).
3. Solvent cleaning.
4. Mechanical abrasion.

In general, solvent cleaning followed by a coat of primer gives the best results on metal surfaces.

It is sometimes desirable to release the foam from the mold surface. This may readily be accomplished by applying a wax coat to the mold surface. Mold release agents that have proved effective are Traffic Wax, S. C. Johnson and Son, Inc., Racine, Wisc., and Perma-Mold 511-02, Brulin and Co., Inc., Indianapolis, Ind.

Jigging

In filling a mold cavity with rigid urethane foam, significant pressures are developed because 5-10% excess foam must be added to insure complete fill. Therefore, the mold surfaces must be supported to prevent distortion of the panel due to the pressure of the rising foam. These pressures may reach 2-4 lb./sq. in.

Venting

To fill narrow and intricate cavities it is necessary that air and foam gases be allowed to escape so that voids are not formed within the foamed article.

Small diameter holes, up to 1/16", positioned at the extremities of the mold surfaces permit sufficient gas release

to fill intricate sections. Larger holes, up to 1", should be provided at the top of the mold to release the bulk of the gases. The smaller vents will seal themselves as the foam gels. The larger holes at the top surface should be closed when the rising foam reaches that point.

Molding Conditions and Techniques

In addition to mixing head and mold design considerations, the manufacture of quality molded parts is dependent on other factors, including mold packing, direction of foam rise within the mold, mold temperature, mold thickness and complexity, and curing conditions.

Packing

In order to assure complete fill of mold extremities and optimum foam properties, a foam charge 5-10% in excess of that needed for an unrestrained foam rise should be used for closed molding as described by Jones⁽¹⁴⁾. Use of too little packing results in non-uniformities and slightly soft foam at the top of the panel. Use of excessive packing results in higher panel densities and higher pressures, which, without adequate jiggling, may distort the mold.

Mold Temperature

Temperatures of 110 to 130°F are desirable with metal molds in one-shot rigid urethane panel molding to insure low panel densities and optimum K-factors. Lower mold temperatures result in high panel density due to loss of heat to the mold.

Generally, with warm (110 to 130°F) molds a panel can be released from the jig in approximately ten minutes. A post-

cure at 150 to 175°F may reduce this time to as little as five minutes.

SUMMARY

In summary, it has been shown that many chemical and mechanical factors affect rigid urethane foam made by the pour-in-place and slabstock techniques. Careful control of these variables is required in the production of product with consistent quality and properties.

TABLE I

ONE-SHOT RIGID URETHANE FOAM MOLDING
FORMULATION AND PROCESS CONDITIONS

Foam Formulation

<u>Ingredients</u>	<u>Parts by Weight</u>
--------------------	------------------------

Component A:

Polyether Polyol ^(a) (460 Hydroxyl No.)	100
N,N,N',N'-tetrakis(2-hydroxypropyl) ethylenediamine ^(b)	8
Triethylenediamine ^(c)	0.3
N,N-dimethylethanolamine	0.5
Dibutyltin dilaurate	0.02
Silicone surfactant	1.5
Trichlorofluoromethane ^(d)	38

Component B:

Nacconate 4040 ^(e)	107
-------------------------------	-----

Processing Conditions

TDI Index (ratio of NCO/total active H)	1.03
Isocyanate Temperature, °F	80
Premix temperature, °F	80
Agitator design	Helical-gear type
Mixing speed, rpm	6000
Output, lbs./min.	36
Mold temperature, °F	125
Cream time, sec.	15
Rise time, sec.	150
Tack-free time, sec.	150

- a. Actol 52-460 Polyol, Industrial Chemicals Div., Allied Chemical Corp.
- b. Quadrol, Wyandotte Chemical Corporation
- c. Dabco, Houdry Process Division
- d. Genetron 11, Industrial Chemicals Div., Allied Chemical Corp.
- e. Industrial Chemicals Division, Allied Chemical Corporation

TABLE II

PHYSICAL PROPERTIES OF ONE-SHOT RIGID URETHANE
FOAM IN MOLDED PANEL (48" x 48" x 2-1/2")

Density, overall panel, lb./cu. ft.	2.35
Density, core, lb./cu. ft.	2.20
Closed cells, %	95
Compression Load, perpendicular to rise, p.s.i.	
at yield point	23
at 10% deflection	30
Compression Modulus, p.s.i.	600
Flexural Strength, p.s.i.	60
Flexural Modulus, p.s.i.	900
Shear Strength, p.s.i.	22
Shear Modulus, p.s.i.	210
Moisture Vapor Permeability, perm-inches	2
Water Absorption, lb./sq. ft., surface area	0.06
K-Factor, cut foam, BTU/(sq.ft.)(hr.)(°F per in.)	
Initial	0.112
After 10 days at 60°C (140°F)	0.123
Dimensional Stability, % Volume Change	
24 hr. at -22°F	< 1
24 hr. at 158°F	< 1
24 hr. at 230°F	4
24 hr. at 158°F, 95-100%, R. H.	8
72 hr. at 100°F, 95-100%, R. H.	1

TABLE III
ONE-SHOT RIGID URETHANE SLABSTOCK FOAM
FORMULATION AND PROCESS CONDITIONS

FOAM FORMULATION

<u>Ingredients</u>	<u>Parts by Weight</u>
<u>Component A</u>	
Polyether polyol ^(a) (460 Hydroxyl No.)	100
N,N,N',N'-tetrakis(2-hydroxypropyl ethylenediamine) ^(b)	4
Phosphorus-containing polyol ^(c) (210 Hydroxyl No.)	4
Triethylenediamine Solution ^(d)	1.25
Silicone Surfactant ^(e)	1.5
Trichlorofluoromethane ^(f)	32
<u>Component B</u>	
Stannous Octoate	0.5-0.7
<u>Component C</u>	
Nacconate 4040 ^(g)	101

PROCESSING CONDITIONS

TDI Index (ratio of NCO/total active hydrogen	1.03
Premix Temperature, °F	65-72
Isocyanate Temperature, °F	65-72
Agitator Design	Martin Sweets Co. VMD-600-Paddle/Pin Agitator
Agitator Speed, rpm	5000-5500
Throughput, lbs./min.	125-150
Conveyor Tilt, Degrees	8-10
Conveyor Cross-Section	38" wide x 24" high
Conveyor Speed, ft./min.	9-13 ft./min.
Cream time, sec.	10
Gel time, sec.	45
Rise time, sec.	90

- (a) Actol 52-460 Polyol, Industrial Chemicals Div., Allied Chem. Corp
- (b) Quadrol, Wyandotte Chemical Corporation
- (c) Vircol 82, Virginia-Carolina Chemical Corporation
- (d) Dabco 33 LV, Houdry Process Div.
- (e) DC 113, Dow Corning Corp.; L-5310, Union Carbide Corporation
- (f) Genetron 11, Industrial Chemicals Div., Allied Chemical Corp.
- (g) Industrial Chemicals Division, Allied Chemical Corporation

TABLE IV

PHYSICAL PROPERTIES OF ONE-SHOT RIGID URETHANE SLABSTOCK FOAM

Density, lb./cu. ft.	1.9
Closed cells, %	95
Compression Load, lb./sq. in., to rise	
at yield point	20
at 10% deflection	28
Flexural strength, lb./sq. in.	45
Shear strength, lb./sq. in.	30
Water absorption, lb./sq. ft. surface area	0.04
K-factor, BTU/(sq. in.)(hr.)(°F/in.)	
(cut foam sample)	
initial	0.115
after 10 days at 140°F	0.130
Dimensional stability, % volume change	
24 hrs. at -22°F	< 1
24 hrs. at 158°F	< 1
24 hrs. at 230°F	2
24 hrs. at 158°F, 95-100% R. H.	7
72 hrs. at 100°F, 95-100% R. H.	2

TABLE V

EFFECT OF INGREDIENT TEMPERATURES ON REACTION TIMES
IN A ONE-SHOT RIGID URETHANE FOAM SYSTEM

	<u>Foam A</u>	<u>Foam B</u>
Premix, °F	70	78
Isocyanate, °F	71	123
Cream, sec.	17	9
Rise, sec.	140	100
Tack free, sec.	145	110

TABLE VI

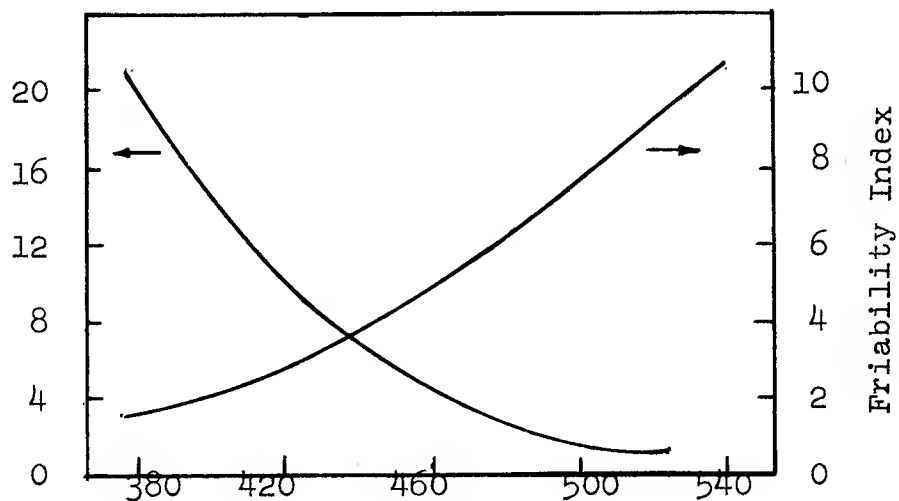
EFFECT OF INGREDIENT TEMPERATURES ON PANEL DENSITY
IN A ONE-SHOT RIGID URETHANE FOAM SYSTEM

<u>Foam</u>	<u>Ingredient Temperatures, °F</u>		<u>Trichloro- fluoromethane Parts/100 Parts Polyether</u>	<u>Overall Panel Density* lb./cu. ft.</u>
	<u>Premix</u>	<u>Isocyanate</u>		
A	77	77	45	2.3
B	87	125	45	2.0
C	77	77	52	2.0

*Panel size - 24" x 24" x 1-3/4"

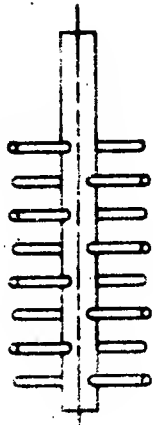
Dimensional stability, %
Expansion after 24 hrs. at 110°C.

FIGURE 1



Polyether hydroxyl number vs. dimensional stability and friability.
(The Friability Index is derived from the indentation (after one hour rest period) attained as a result of a 20-in.-lb. impact by a 1-in. diameter cylinder).

FIGURE 2
TYPICAL AGITATOR DESIGNS



PIN TYPE
LOW SHEAR

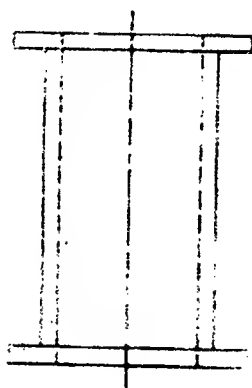


HELICAL GEAR TYPE
HIGH SHEAR

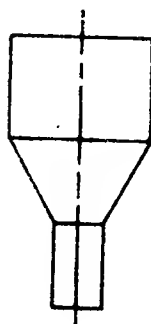
FIGURE 3
TYPICAL MIXING CHAMBER



AGITATOR
(Helical Gear Type)



HOUSING



OUTLET ORIFICE

REFERENCES

1. Smoluk, G. R., Modern Plastics, 42 No. 7, 129 (1965)
2. Modern Plastics, 43, No. 3, 105 (1965)
3. Hudgens, H. R., J. Cellular Plastics, 2, No. 6, 316 (1966)
4. Bruce, H. J., J. Cellular Plastics 2, No. 6, 306 (1966)
5. Seele, M., Plastics Tech., 9, No. 1, 42 (1963)
6. Kaplan, M., Plastics Tech. 10, No. 8, 38 (1964)
7. Technical Bulletin TS-16, "Rigid Urethane Foam", National Aniline Division, Allied Chemical Corporation
8. Kaplan, M., Dickert, E. A., Himmler, W. A., Hipchen, D. E., Silverwood, H. A., and Zettler, R., "Molding of One-Shot Rigid Urethane Foam", Presented at the 50th National Meeting of the American Institute of Chemical Engineers, Buffalo, New York, May 1963; Chem. Engr. Prog. 59, 33-38 (1963)
9. Hipchen, D. E. and Silverwood, H. A., "Rigid Urethane Slabstock by the One-shot Technique", Presented at the Foam Plastics Conference, Natick, Mass. 1966.
10. Einhorn, I. N., "Spray Application of Rigid Urethane Foam", The University of Michigan Engineering Summer Conference Cellular Plastics, 1964.
11. Snyder, R. B. and Pang, F. S., Cellular Plastics Division, 7th Annual Technical Conference Proceedings, New York City, April 1963.
12. Kaplan, M., "Thermal Conductivity of Cellular Urethanes -- Theoretical and Practical Aspects", Wayne State University Polymer Conference Series -- Cellular Plastics, 1966.
13. Stewart, A. S., "Types of Urethane Foam Equipment" and "Urethane Foam Processing", The Wayne State University Polymer Conference Series -- Cellular Plastics, 1966
14. Jones, R. E., Plastics Tech., 7, No. 10, 27 (1961)

10214-15

MICROWAVE CURING OF CELLULAR PLASTICS.

W. J. Hoskin B.Sc.Eng.

Elliott Electronic Tubes, Ltd.

January, 1967

MICROWAVE CURING OF CELLULAR PLASTICS.

10214-15

Introduction.

The use of electrical energy at frequencies other than the conventional 50/60 cycles for industrial heating has resulted in an investigation being made into the properties of electrical energy over a wide spectrum of frequencies. Fig. 1., shows the normal electromagnetic frequency spectrum and it may be seen that this covers normal power frequencies, the radio bands, microwave bands, infra red, visible light, ultra violet, X-rays and finally gamma radiation. All these frequency bands have their own particular characteristics and it is often advantageous to examine the effects on chemical compounds and chemical reactions of electromagnetic radiation produced at a number of widely differing frequencies; for example, it is already well known that gamma radiation can effect chemical changes in many compounds and experience with microwaves has indicated too that certain chemical effects in addition to heating effects take place under the influence of high alternating electrical field densities.

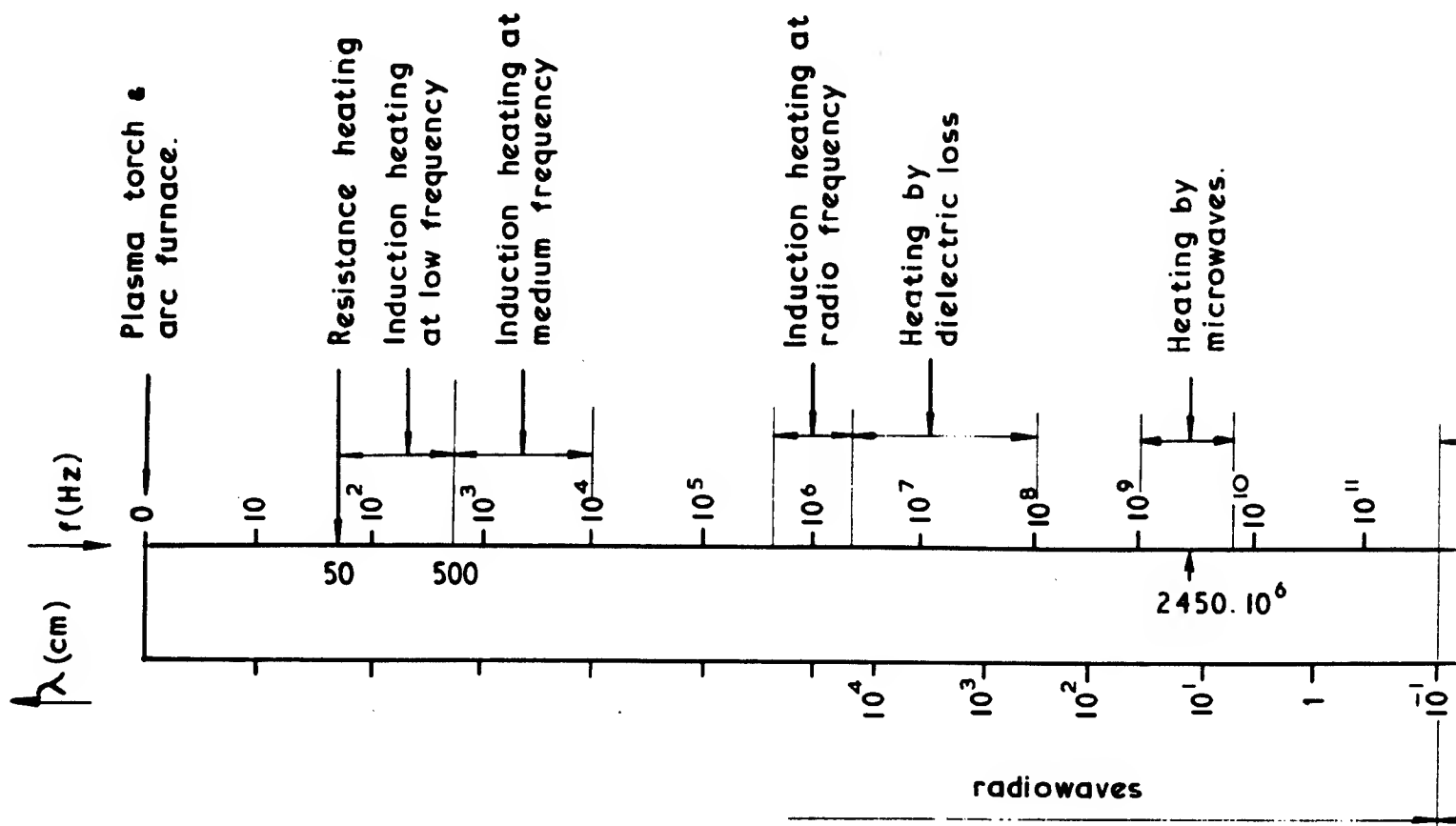
It is intended to discuss in more detail the use of microwave energies in connection with cellular plastics and before dealing with the effect of microwaves in particular it is convenient to examine methods of heating over a wide frequency range. Heating by electrical energy at very low frequency is merely by I^2R losses but at the frequency increases it will be noted that in addition

Contd

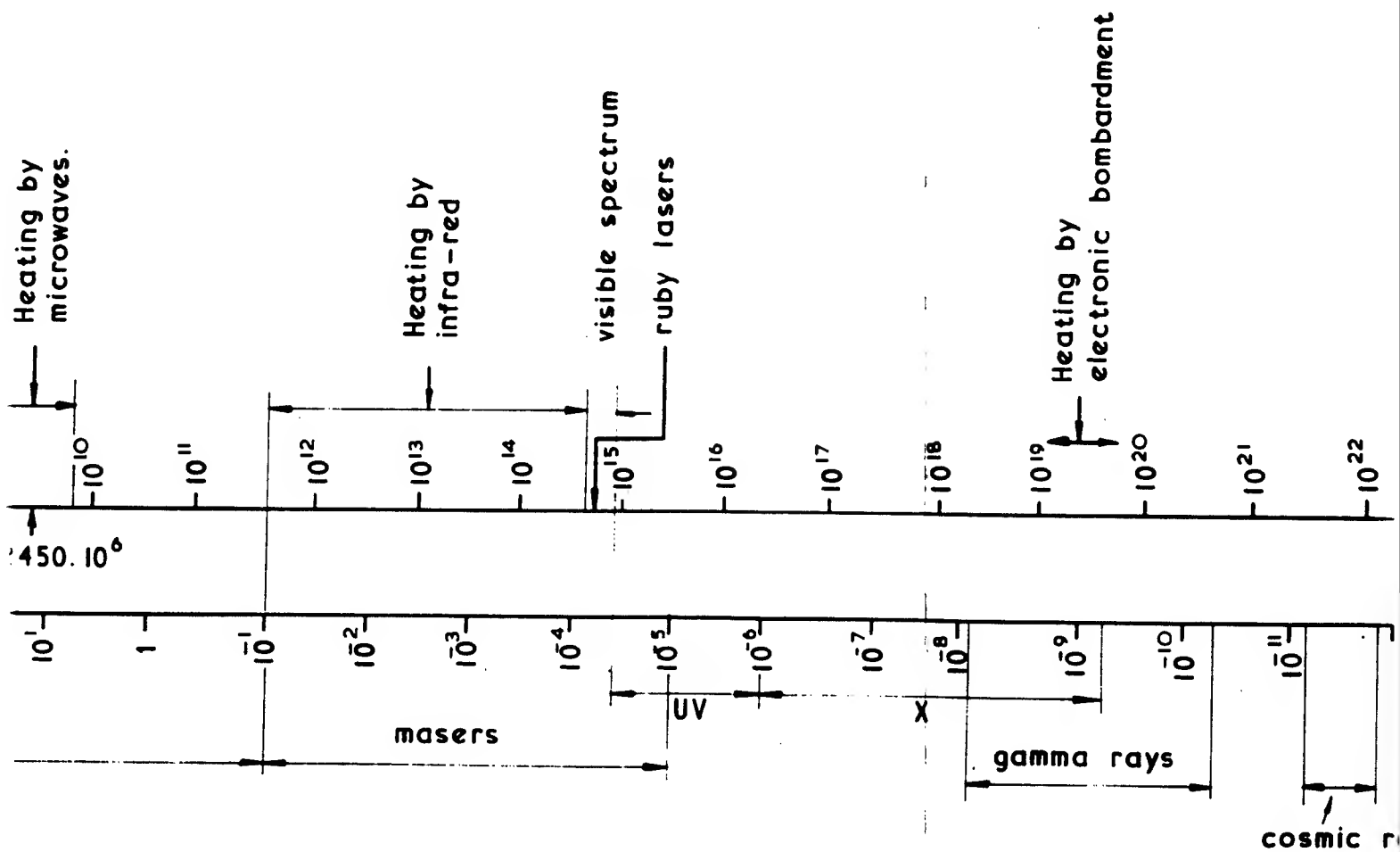
to normal heating of a conductor by this means the magnetic field produced by passage of the current is capable of coupling with any electrical conductor placed close to it and under these circumstances the action may be compared to that of a transformer with a short circuited secondary. This results in the generation of high currents in this electrical conductor which will result in considerable heating, although again this is due to I^2R losses. In order to utilise this effect frequencies between 50 and 100 Kc/s are usually chosen and it is usual to wind the conductor through which the current is passing into the form of a coil. The object to be heated is placed within the coil to ensure maximum coupling to the magnetic field.

As the frequency is increased further however it becomes difficult to feed power into a high inductance coil such as that normally used for induction heating and eventually it becomes impossible. On the other hand it is known that imperfect di-electric materials if subjected to high alternating electrical stress will generate considerable heat within themselves and it is possible to use higher frequencies, usually at 28 mgc/s for heating di-electric materials of specific size and shape by subjecting them to high alternating electric fields. This form of heating is known as heating by di-electric loss and the energy is usually fed to the di-electric by means of parallel plates between

Contd



193



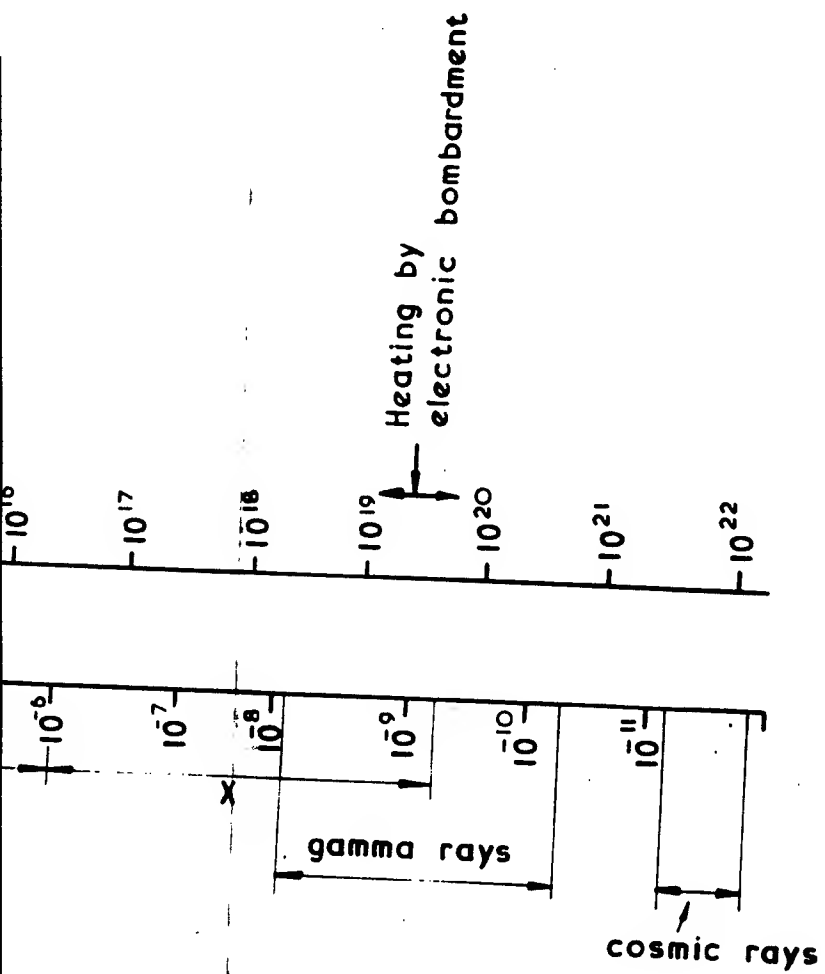


Fig 1

which the di-electric is placed.

As the frequency is further increased, problems of feeding energy to parallel plates become difficult and ultimately impossible, yet at higher frequencies still, new methods of feeding power to di-electric materials by using waveguides can be devised and this is now named microwave heating. Since it is basically di-electric heating, it is convenient to look at a very simple explanation of di-electric heating and to examine the formulae derived for the electrical parameters which determine the heating effect so that the effects of frequency, voltage stress, di-electric constant and the loss angle can be determined.

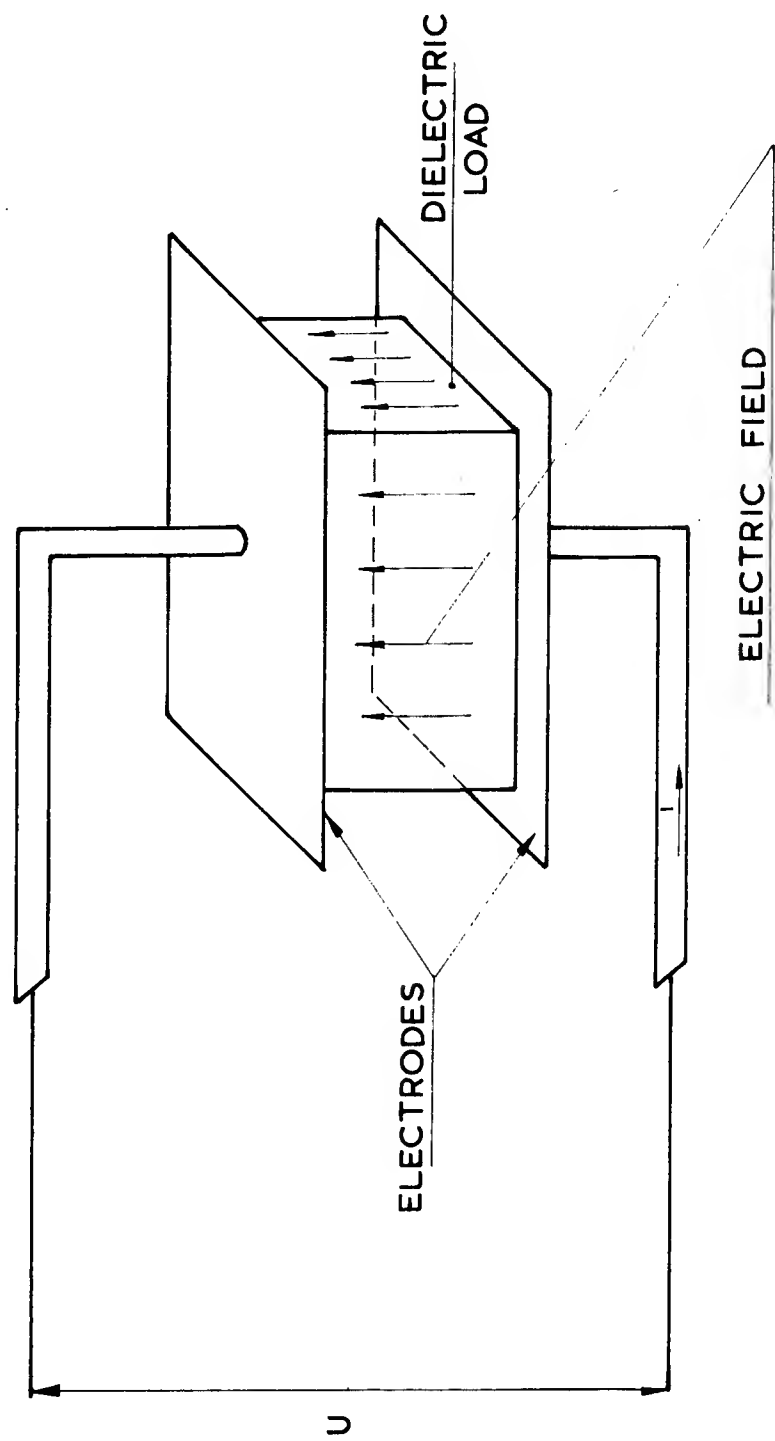
Di-electric Heating.

Heating is obtained at radio frequencies in a di-electric material by applying an alternating electrical field of high intensity across the material. This field is usually generated across the plates of a capacitor in a tuned circuit and the material to be heated is placed between those plates. This arrangement is quite efficient and enables a uniform amount of heat to be generated in a homogeneous material.

Consider a parallel plate condenser made as shown in Fig.2., between the plates of which is placed a block of di-electric to be heated.

Contd

FIG. 2.



The power P generated in the capacitor is:-

$$P = VI \cos \phi$$

When

V = applied voltage

I = current

ϕ = angle of lag

When the capacitor is perfect $\phi = 90^\circ$, $\cos \phi = 0$ and $p = 0$
 ϕ is never 0 in practice however and the angle $\phi = 90^\circ - \delta$
 where δ is known as the loss angle.

Consider the vector diagram in Fig. 3., the power now generated in the capacitor will be $VI_c \tan \delta$, since $\tan \delta = \frac{I_r}{I_c}$.

$$\text{Now } I_c = V\omega C = V \cdot 2\pi fC$$

when $\omega = 2\pi \times \text{frequency } f$.

$$I_r = \frac{V}{R}$$

C = capacitance of condenser

$$\therefore \tan \delta = \frac{\frac{V}{R}}{V\omega C} = \frac{1}{\omega RC}$$

$$P = \frac{V^2}{R}$$

$$\therefore P = V^2 \tan \delta \cdot 2\pi fC.$$

For a parallel plate condenser, an approximate value for the capacitance can be obtained from the expression

$$C = 0.08842 \frac{S}{d} K$$

where S = area in sq. cms.

d = distance between plates in cms.

K = di-electric constant

Contd

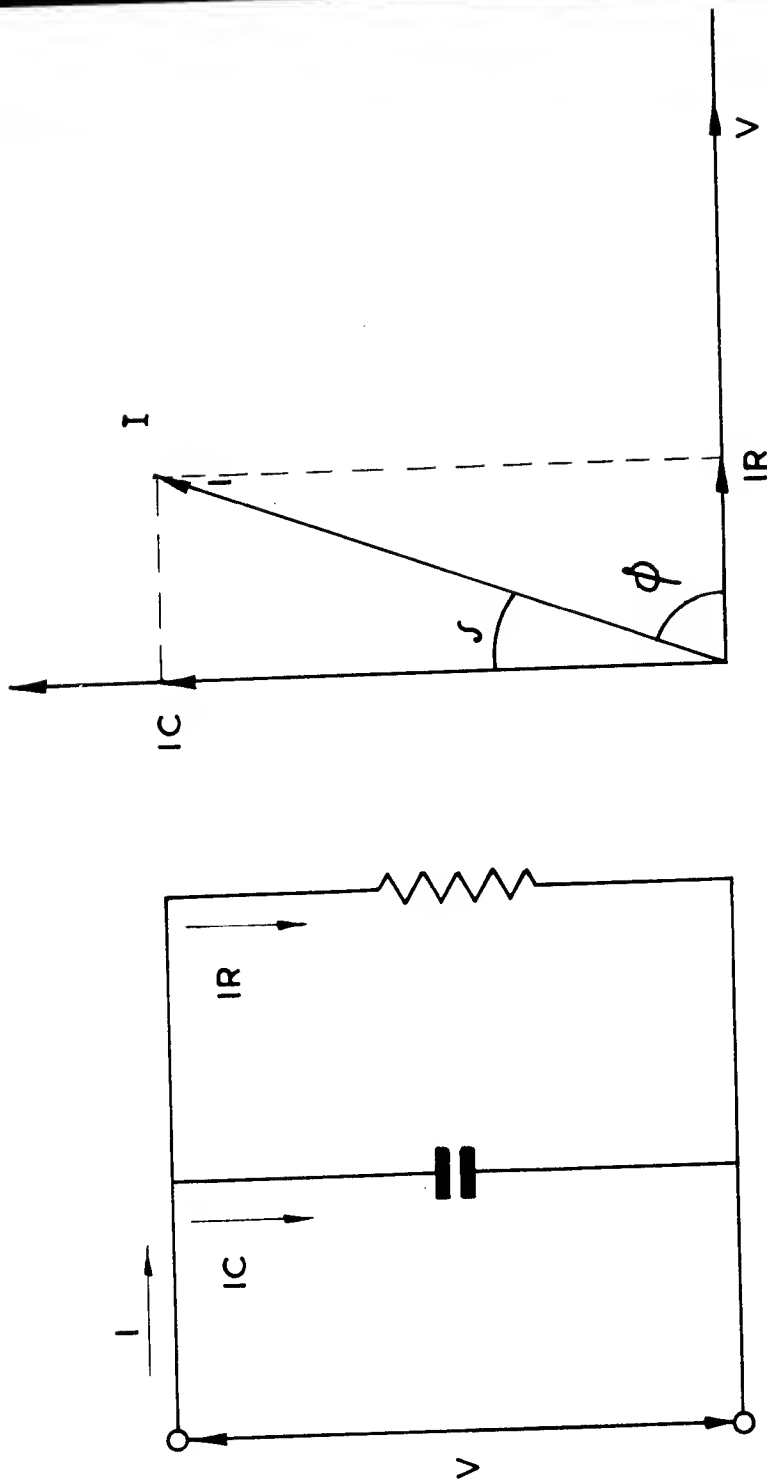


FIG. 3.

$$P \text{ now becomes } V^2 \tan \delta \cdot 2\pi f \cdot 0.0884 \frac{S}{d} K$$

$$= 0.555 \times 10^{-12} V^2 K \tan \delta f \cdot \frac{S}{d}$$

On the assumption that 0.239 watt seconds are equivalent to one calorie and ignoring the heat losses due to radiation and conduction, the temperature T after t seconds will be given by

$$T = T_o \div \frac{0.239 P.t.}{M.Sp.}$$

Where

T_o = Initial temperature

M = Mass of the di-electric

Sp = Specific heat of the di-electric.

Transposing

$$T = T_o \div \frac{0.1365 V^2 K \tan \delta f S t}{10^{-12} d M.Sp.}$$

It is clear from an examination of this expression that the power dissipated depends on (a) the square of the applied voltage

(b) the di-electric constant

(c) the frequency

(d) the loss angle

It must also be noted that the loss angle is generally frequency dependent as is the di-electric constant. These properties may also be temperature dependent and thus the rate of which power is absorbed may vary at any time during a heating cycle.

It is not generally practicable to increase the voltage considerably since the di-electric strength of the material to

Contd

be heated may be very low and breakdown may occur. A value of voltage has to be chosen which gives an adequate safety factor.

The loss angle usually increases with frequency so that it is desirable to increase the frequency if practicable.

Unfortunately, the frequency limits the physical dimensions of the plates of the condenser and Absil* gives a formula for the greatest dimension of the condenser L

$$L < \frac{\lambda}{16\sqrt{K}}$$

In general it is possible to compare the relative merits of various di-electric materials for this heating process by comparing the product of their di-electric constants and loss angles - the loss factor.

Some of the disadvantages of di-electric heating are:-

- (a) The capacitor and hence the di-electric cannot be far from the inductance and hence the heating operation must be carried out in close proximity to the power supply.
- (b) The di-electric must be homogeneous, since the value of the capacitance at any point is dependent on the di-electric constant. If the material is not homogeneous considerable variation in temperature will occur throughout the di-electric material.

Contd

- (c) The plates of the capacitor may have to be shaped or placed at an angle to each other to accomodate various shaped articles thus reducing flexibility when small quantities of different materials are being processed.
- (d) Although the lowest possible voltage is generated across the plates consistent with satisfactory operation, many products cannot be heated by this means because of voltage break down of the material.
- (e) Since the voltage is high, the chance of sparking occurring is high and inflamable materials have to be treated cautiously.

The advantages of this system are many however. Materials of poor thermal conductivity can be heated uniformly and since the power is generated only within the material, the process is very efficient, in addition the thermal conductivity of the material does not determine the temperature rise at the centre of the material as is the case when radiant heating is used.

Materials having a high water content can be dried efficiently by this means subject to the materials being of the correct form. It must be noted from the formulae already developed that the rise in temperature is dependent on and is proportional to the applied power. In order to keep the V^2 in the equation as low as possible it is essential that one of the other variables

Contd.....

are changed and it is convenient to increase the frequency particularly since the loss angle δ usually increases with frequency as does the di-electric constant K. There is therefore a very considerable advantage to be gained from increasing the frequency.

Microwave Heating.

The basic principles of microwave heating are similar to those of di-electric heating but there are several major differences in the method of operation which overcome many difficulties and disadvantages apparent with conventional di-electric heating. When the frequency is increased from 100Mc/s to 2,000 Mc/s the method of introducing the energy into the di-electric differs considerably from that used in di-electric heating. The di-electric generator consists of a power supply and an oscillator tube which supplies radio frequency power to the inductance and capacitance of the tube circuit. In the case of one form of microwave generator the power supply merely consists of a unit which transforms the voltage from the mains electricity supply to 7,000 volts which is then fed to a magnetron oscillator. A magnetron oscillator contains within its vacuum envelope the tuned circuit and delivers the energy via an aerial and a waveguide to the applicator

The waveguide consists of a rectangular section of brass, aluminium or copper tube. The applicator for microwave energy

Contd

can take many forms.

One simple form consists of a box whose dimensions are so chosen that for the frequency generated, the box becomes a resonant circuit. The power is then fed from the magnetron to this resonant cavity by means of a waveguide which can be of any length. The di-electric material which is to be heated is placed within the metal box but while in the case of di-electric heating, the metal plates have to be in close proximity to the di-electric (since the di-electric and the metal plates form the capacitance), in this case no metal need be close to the di-electric material, and the shape of the material is unimportant.

The characteristics which determine the amount of heat generated in the material are similar to that for di-electric heating, in that the loss factor in general is a good guide as to whether or not the material can be heated. At these frequencies however the loss angle is considerably greater than that at 100 Mc/s and thus for the same amount of energy absorbed in the material the voltage stress can be decreased considerably and the chances of breakdown reduced. Furthermore, in the case of microwave heating the electrical potential is developed in the material by means of a travelling field pattern. Since this field pattern is not static and moves with some considerable rapidity the chances of voltage breakdown of the di-electric material are much less.

Contd

It has been found that because of these properties, materials which cannot be heated by conventional di-electric heaters can be heated satisfactorily by microwaves. Fig. 4., shows a simple resonant cavity and power supply. It should be noted that this type of applicator avoids most of the disadvantages present in di-electric heating and indeed allows a system to be used which is very simple.

For industrial purposes in the United Kingdom four frequencies have been assigned to microwave heating. They are 915 Mc/s, 2450 Mc/s, 5800 Mc/s and 22,500 Mc/s. It is important to note that the application of microwave energy is comparatively simple and is effected merely by passing the energy by a wave guide into an applicator which is usually a resonant box or cavity which is large enough to hold the material to be heated and which due to multiple reflections from the walls produces a pattern of energies within the cavity which can be adjusted to provide uniform heating for a uniform di-electric placed within the cavity.

There are however certain difficulties with a simple cavity and in order to assess the possibility of using the cavity resonator for use with plastics it is essential to know in some detail the problems that may be encountered in providing uniform heating. It had been thought that provided a simple enclosed metal box had a resonant frequency which matched in frequency the generator

Contd

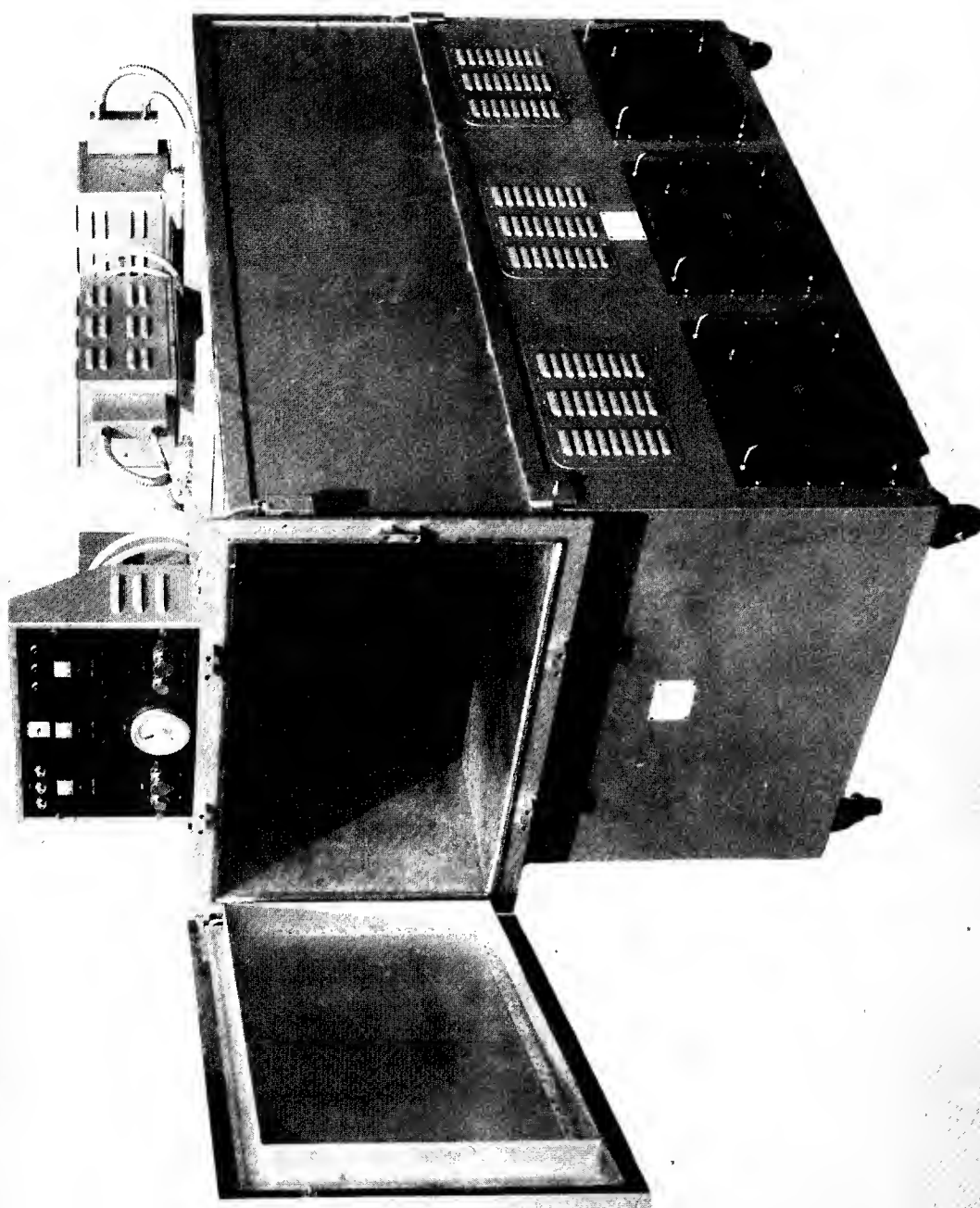


Fig. 4.

then a large number of modes would be present and that a uniform field inside the box would be sustained. Practical experience has shown that this is not true and that it is quite difficult to obtain a cavity where the electrical field is uniform and which enables di-electric materials to be uniformly heated. It must be noted also that the size of the object and its di-electric constant when placed within the cavity alters the electrical size of the cavity resonator and thus detunes the resonator. This is further complicated by the fact that certain parameters change with temperature and it is obvious that the cavity can be detuned during the heating cycle. This will result in a reduction of power input due to poor coupling between the load and the magnetron. It is often necessary therefore to design a cavity and subsequently modify it experimentally in order to determine the optimum dimensions for any given product. On the other hand it is possible to apply certain corrective measures which can help to ensure uniformity without the necessity of considerable mechanical complication. As an example suppose a simple rectangular cavity is chosen with its resonant wave length as given by the following formulae:

$$1/\lambda_{\text{res}} = \frac{1}{2} \left[(m/a_x)^2 + (n/a_y)^2 + (p/a_z)^2 \right]^{1/2}$$

in which a_x , a_y , a_z , = the dimensions of the oven space

m , n , p , = the integers.

Contd

For each value of the integers it is possible to obtain a resonance but the interaction of the waves within the cavity results in a field pattern which contains points of maxima and minima electric field and which thus may result in uneven application of energy to the di-electric material. It is essential therefore that the number of modes should be increased to the maximum possible to ensure the most uniform field pattern within the cavity and it is possible to carry out calculations which show the number of modes which can be determined for any one resonant frequency. It is also important to note that the larger the size of the cavity the smaller the number of mode changes possible for small changes in cavity dimensions. Nevertheless it is true that for a given target dimension it is always possible to determine dimensions close to this target which will produce the maximum number of modes. In general these dimensions should always be chosen. Since the fact of introducing di-electric material into the cavity materially changes the electrical parameters this design may not produce adequate uniformity and it is often therefore essential to carry out further adjustments. These usually consist of either the addition of a simple field stirrer which causes movement of the maxima and minima positions of the electric field, that is, it alters the phase of the incoming power without altering the coupling and hence is a simple non-

Contd

uniform loss less di-electric body which changes position at the input of the power, or it consists of a metallic vane which is made to rotate close to the power entry point and which changes the direction and usually the amplitude of the input power.

A more complicated system consists of a supplementary cavity feeding the main cavity via a number of coupling windows which are alternately covered by some form of di-electric stirrer. In addition, for small installations the material to be heated is often rotated but it is an added complication and is generally unnecessary if the cavity is correctly designed.

Fig. 5., shows a simple cavity having both a stirrer and turntable.

In order to restrict the effect of dimensional change on the number of modes Fig. 6., and 7., show the effect of changing the length of one dimension to a standard cavity on the number of modes which can be produced.

During practical tests on various materials it has become apparent that when large volumes of di-electric material are to be heated in large cavities a good match can be obtained between the magnetron and the cavity to produce efficient heating. However should the charge in the cavity become small in relation to the cavity problems occur due to difficulties in coupling the electromagnetic radiation into this small load.

Contd

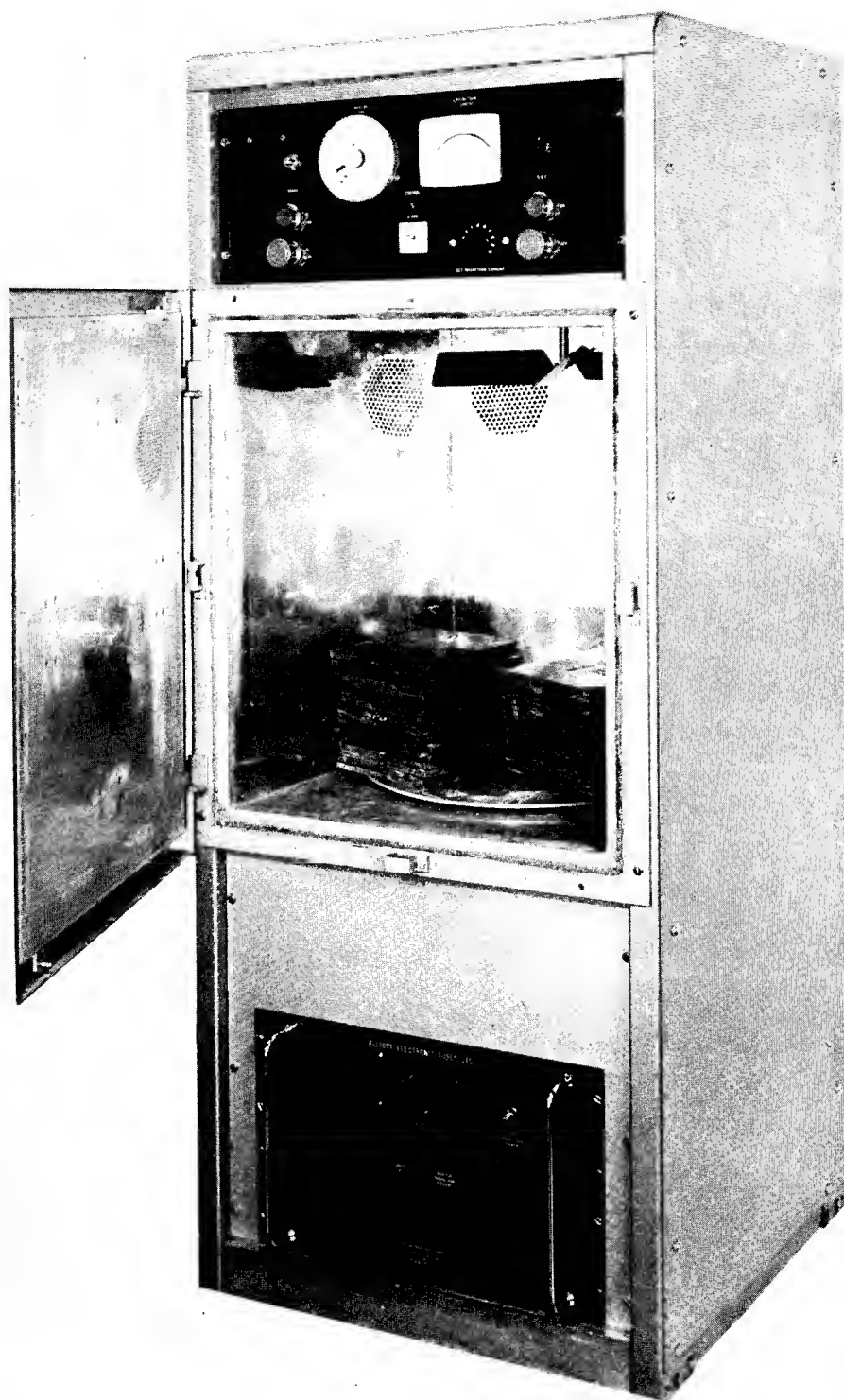
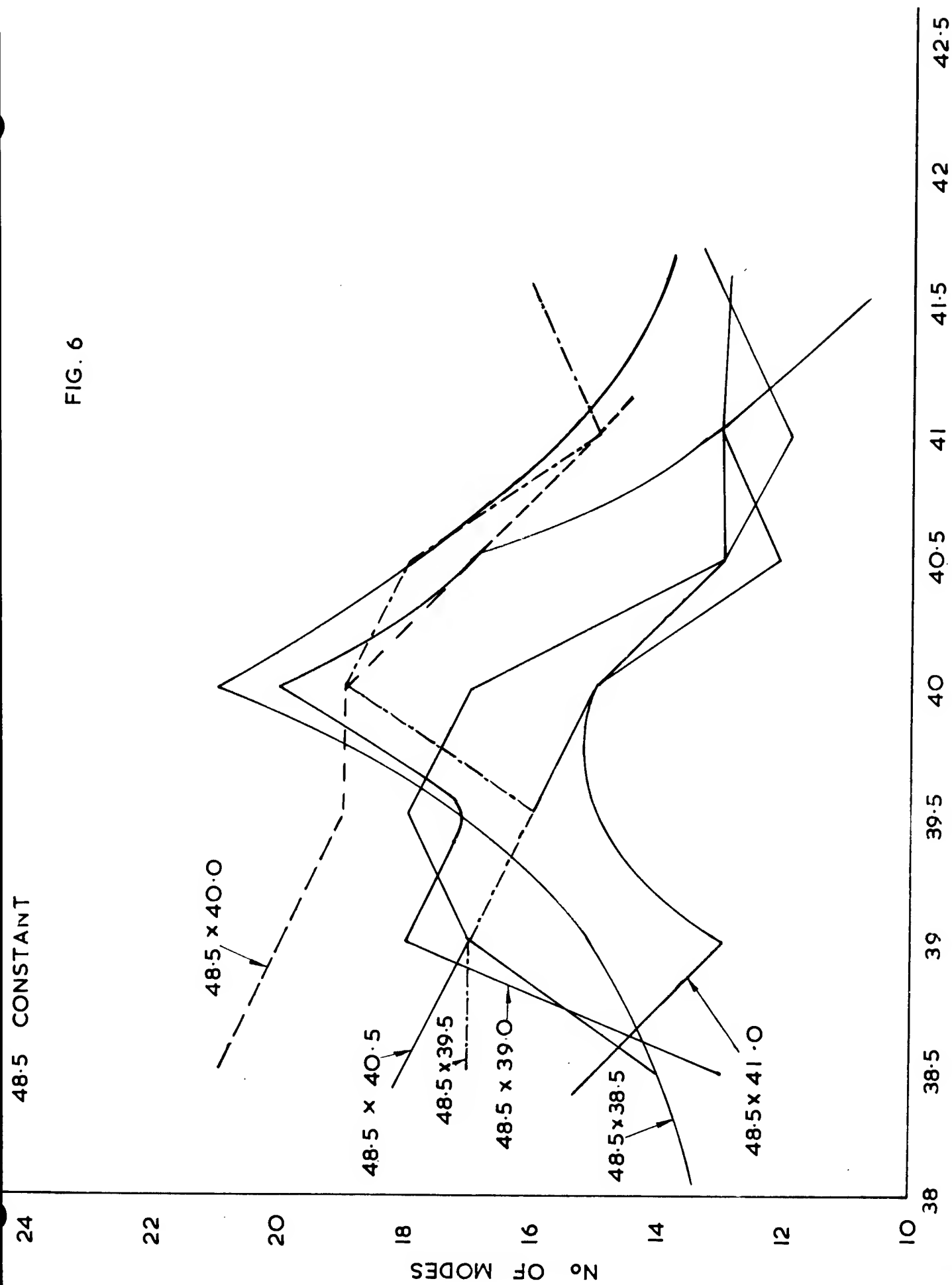


Fig. 5.

FIG. 6



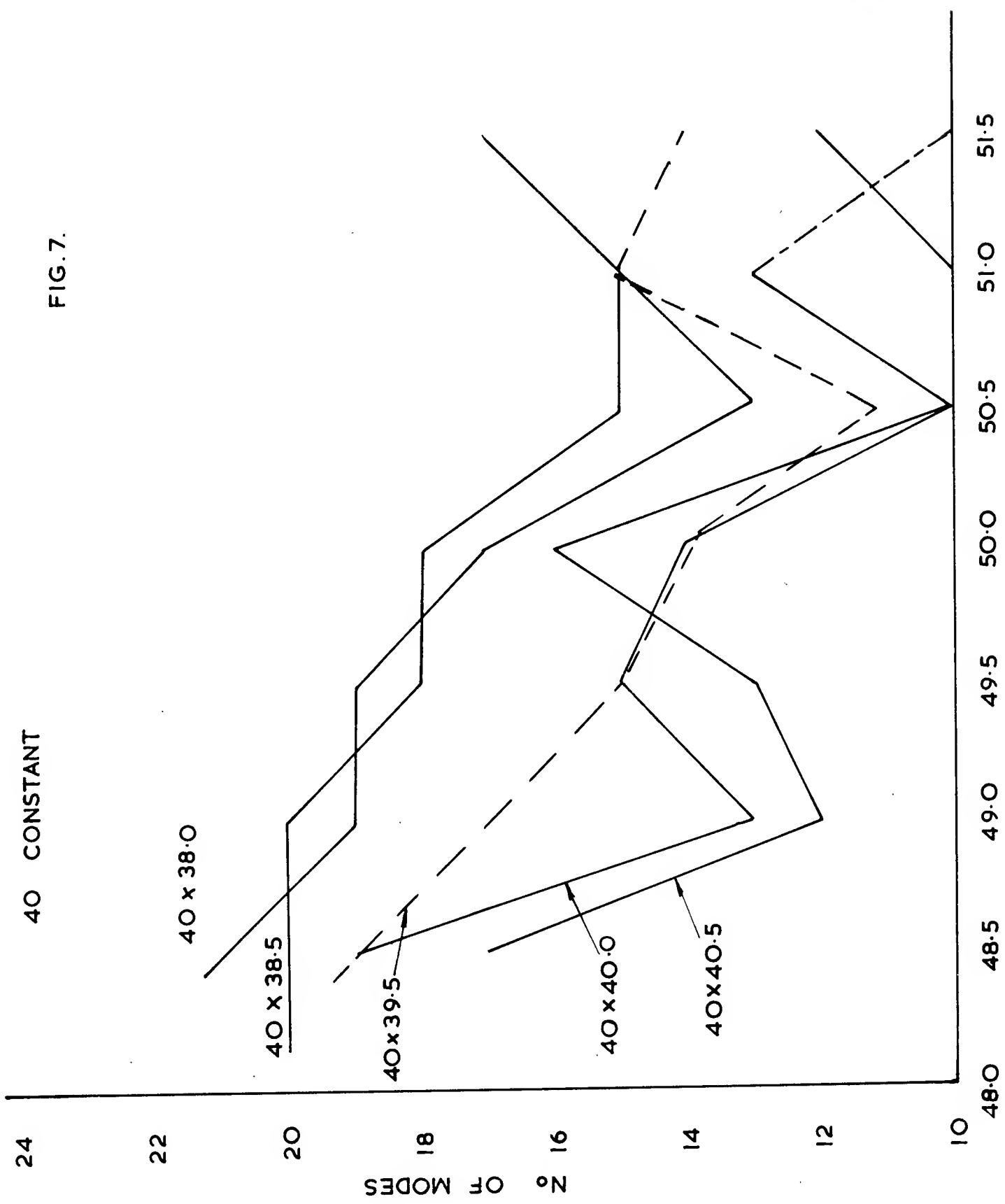


FIG. 7.

If we consider a small load in a large cavity, then at any instant there is a large part of the electric field which is playing no useful part in heating the load and which nevertheless contains considerable energy. Since at these high frequencies currents induced in the walls of the cavity do not penetrate much beyond the surface it is not easy to arrange for this energy to be dissipated. If care is not observed high potentials may build up which will eventually cause sparking. If the energy is reflected back toward the magnetron it is easily possible to cause overheating of the magnetron window and its eventual destruction. It is therefore necessary in the design of such devices to ensure that high powers can never be reflected back towards the magnetron and that coupling between the load and magnetron must be reasonably good at all times. To prevent inadequate loading it is sometimes the custom to introduce lossy materials in the walls or corners of the cavity but although this reduces considerably the chances of magnetron damage the operating efficiency of the process is reduced since these loads are always present and absorb energy even when the charge is in position.

A high power isolator is a convenient though expensive device to prevent reflection back into the magnetron and under certain very difficult conditions where the cavity loading changes from near zero to maximum under operation, this is often the only

Contd

satisfactory solution. In this case reflected power is fed away from the magnetron into a load designed to dissipate the heat generated without damage.

It has been stressed that care has to be taken to obtain the maximum number of modes for uniform heating but a complication arises when the cavity becomes very large. Supplementary modes may be set up which cannot always be suppressed and which may vary considerably with the di-electric properties of the material being heated. It may well be impossible to sustain the field pattern required under such circumstances and specially made suppressors may have to be inserted into the cavity at specific points. Unfortunately they have to be positioned by trial and error.

The temperature rise in a di-electric load may not be uniform even if the field within the cavity is uniform, since the energy transfer to a molecule on the surface may well not be the same as that within the body. On the other hand heat loss by radiation from the surface may cause the surface temperature to be much lower than the remainder of the di-electric. Since microwaves can be focussed by suitably shaped di-electric materials certain geometrical shapes can have marked patterns of uneven temperature rises even though the field pattern using other shapes may be excellent. Figs. 8, 9, 10, and 11., show some of these effects.

Fig. 8., shows a triangular sample in Agar (a material having

Contd

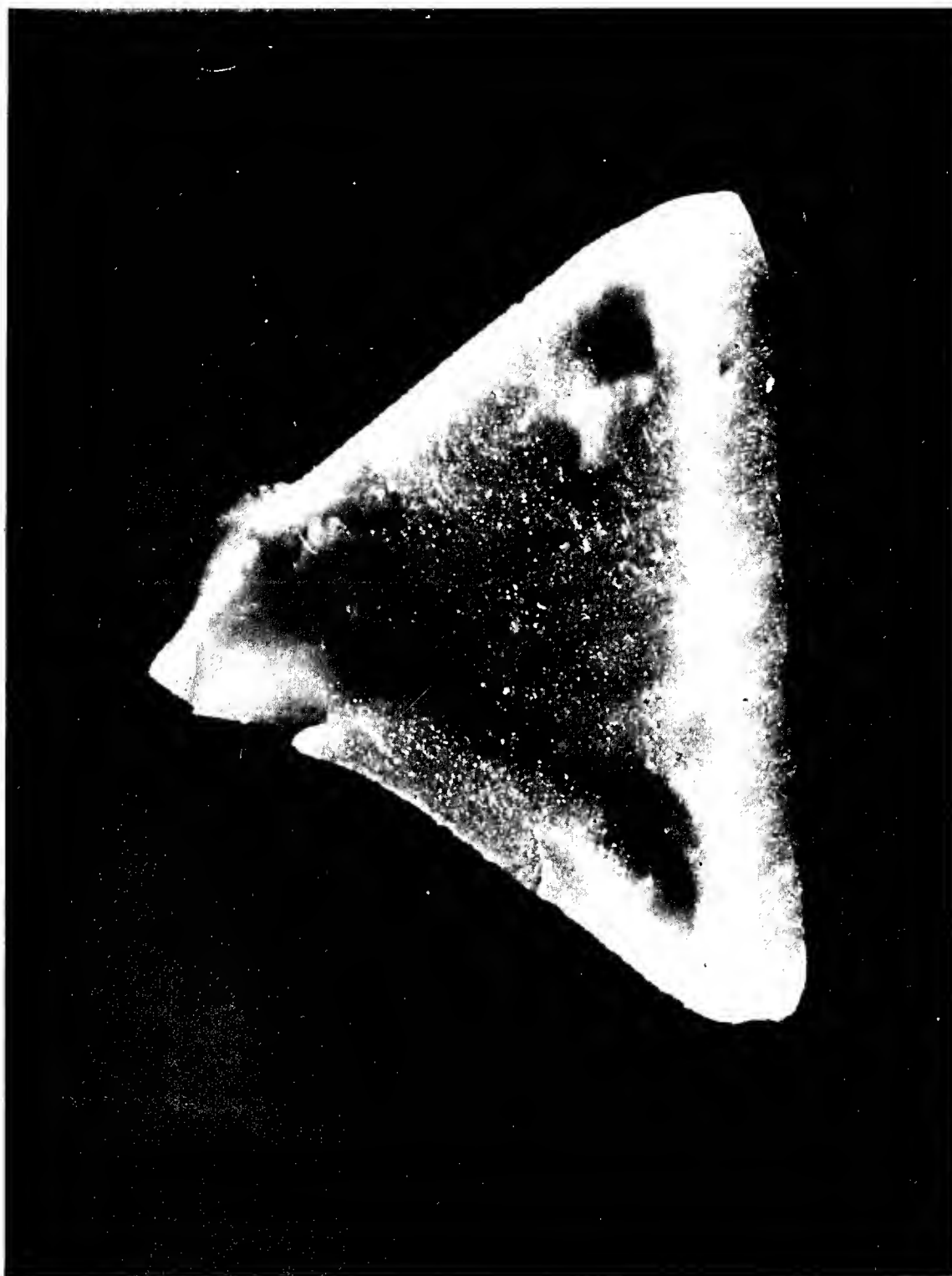


Fig. 8.



Fig. 9.

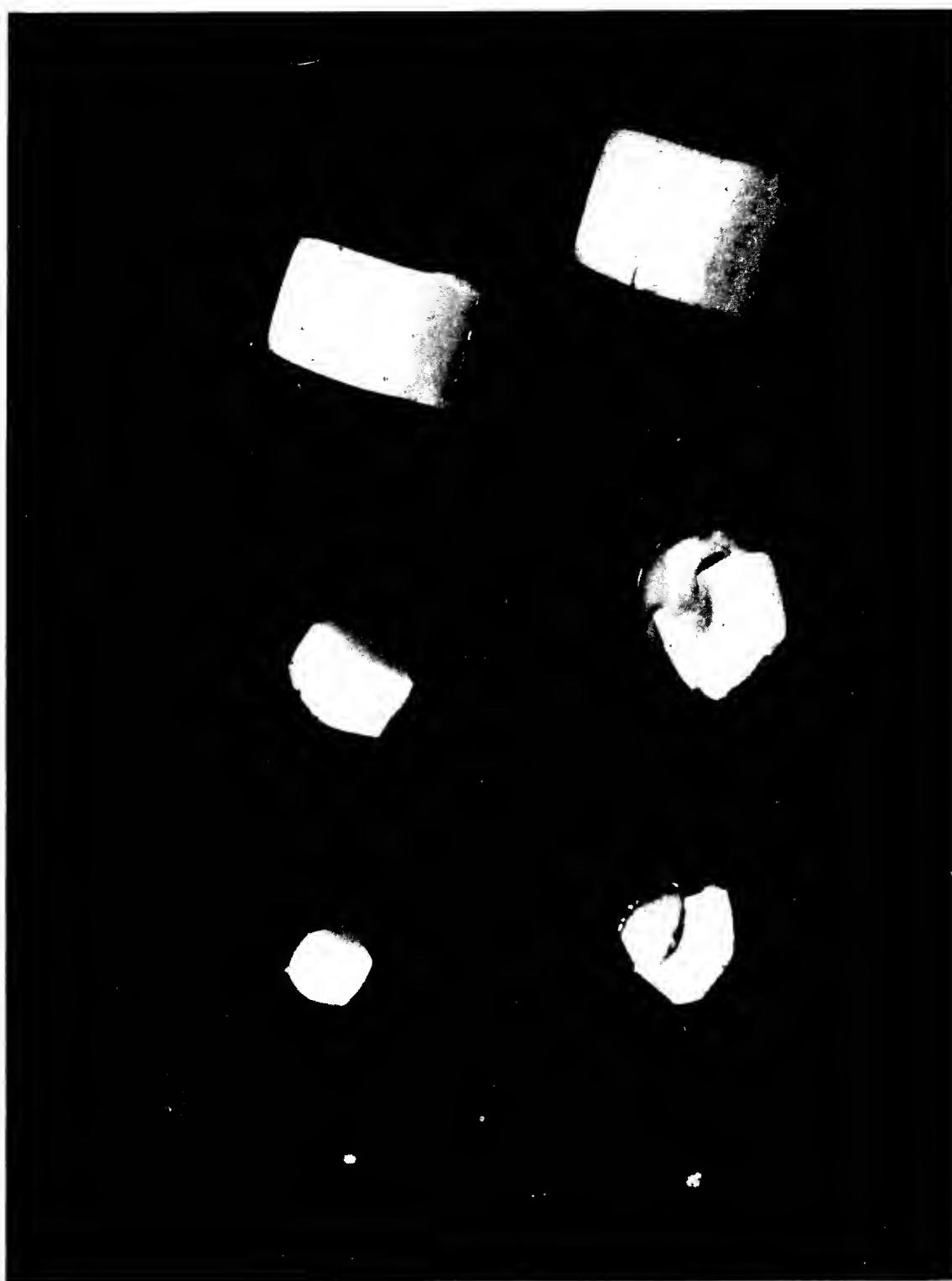


Fig. 10.

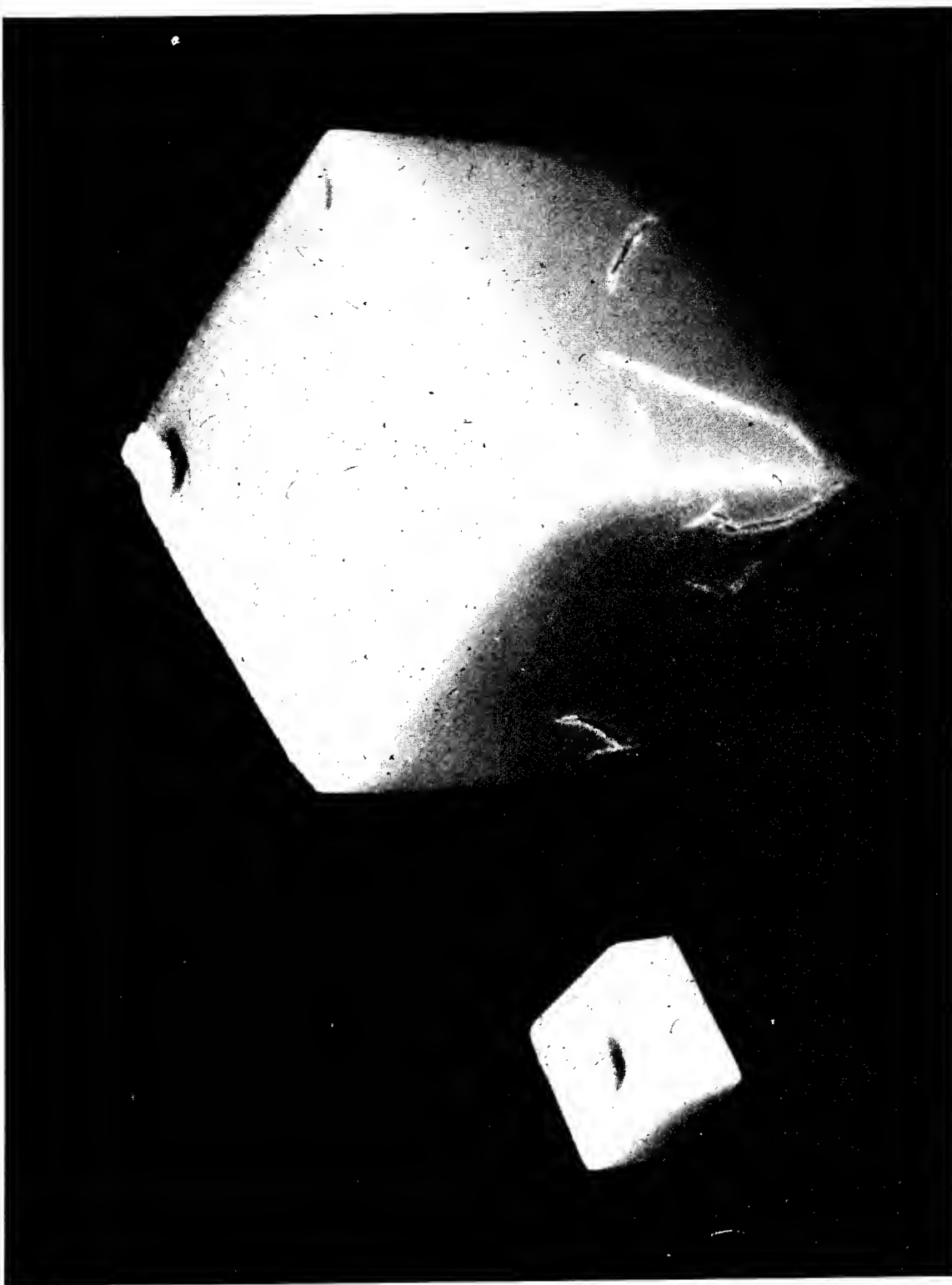


Fig.11.

almost identical di-electric properties to water) with sides about 7 cms and with a thickness of 0.75 cms. This has been heated in a cavity in which the uniformity has been very carefully checked and adjusted, and melting point occurred as shown. Fig. 9., shows what was originally a sphere which has been cut open to show the melted centre.

Fig. 10., shows 8 cubes. Four are untreated whilst four have been placed in a cavity and heated. The smallest cube with sides of 0.2cms was unmelted; the two medium size cubes melted and these reached over 92°C , the melting temperature of Agar, whilst the largest, a cube of 2 cms side did not melt. Fig. 11., is also of two cubes, the smaller, which has sides of 2.5 cms has been sliced across the centre whilst the larger of 10 cms sides has had a layer removed from the top to display the melted corners. This pattern change occurs when the side dimensions are about 4 cms.

The fact that so much of the work is carried out empirically is probably one of the reasons for the slow development of microwave heating and is certainly one of the reasons why application costs are high. It is important to note that once a design has been completed, repetition is reasonably trouble free and problems in manufacture are few.

Although previous remarks may seem to show the impracticability of microwaves industrially, nevertheless experimentation and now

Contd

production equipments which have been in operation for two or three years show that applications of this technique can have beneficial effects on the processing and process costs.

Perhaps the earliest industrial production equipment was made for the curing of flexible polyurethane foam mouldings and although the chemistry has now changed so that many of the advantages of the use of microwaves have disappeared the flexibility of the microwave heating process is demonstrated by this application.

It so happens that uncured foam is extremely lossy whilst cured foam is no longer so when cold. It would appear therefore that the system is self adjusting and that if a mould containing uncured polyurethane foam was placed in a microwave heater, if the mould was transparent to microwaves the moulding would heat until cured when as it then became loss free, the heating would cease. Unfortunately in order to obtain mould release and to cure the surface, the surface has also to be raised in temperature and therefore although the mould must be transparent to microwaves, it must have an inner skin which will heat sufficiently to melt the release agent and ensure a good skin cure. In addition the mould must have good mechanical strength, be stable, cheap to manufacture and have long life. The first moulds were made with epoxy resin loaded with metal powder. The addition of metal powder was made to adjust the loss factor to the value desired.

Contd

Fig. 12., shows the general construction. To prevent loss of heat by radiation the exterior of the mould was sprayed with rigid polyurethane foam. The procedure adopted for moulding was the following:-

- (1) Apply release agent.
- (2) Heat mould to 50°C (either by microwaves or infra red).
- (3) Introduce the polyurethane mixture.
- (4) Close the mould.
- (5) Wait for the chemical reaction to form the foam to take place (Approximately one minute).
- (6) Heat by microwaves in cavity.
- (7) Remove moulding.

The process which apparently took place was:-

- (a) the exotherm heated the centre of the foam and caused some cross linking
- (b) the microwaves commenced to heat the inner wall of the mould and all the uncured foam
- (c) when the cross linking was completed the foam became almost loss free and all the power was absorbed by the mould walls and these rapidly increased in temperature, resulting in melting of the release agent. Since the mould was so well insulated, the foam remained at temperature for some time and removal could be delayed if need be.

Contd.....

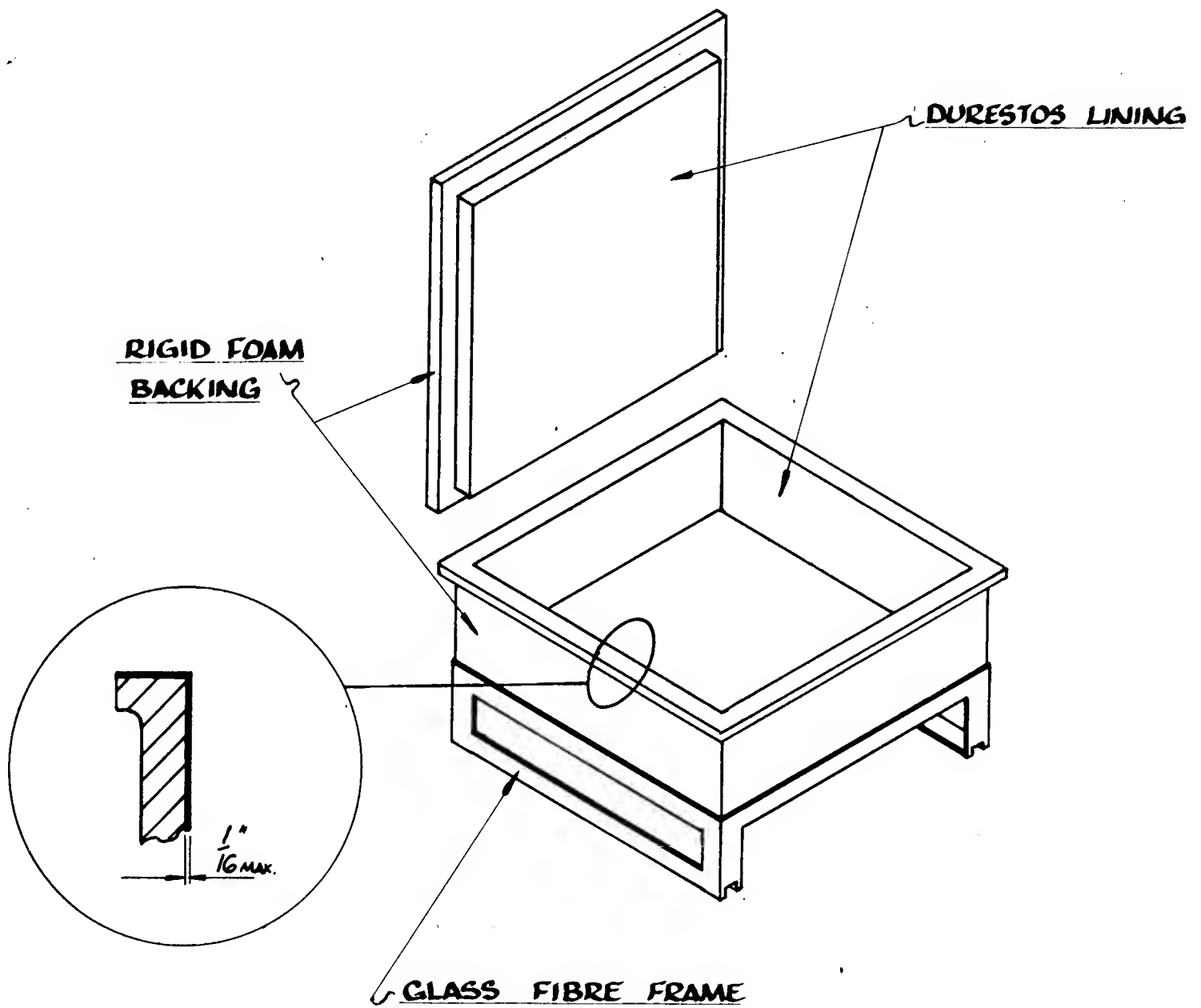


Fig. 12.

The amount of microwave power had a considerable effect on the time the mould needed to be in the microwave cavity and although the total process time varied little from five minutes for a 900 gramme moulding, up to three minutes of this could be waiting time after removal from the microwave cavity before removal from the mould. Fig. 13., shows a typical time-power curve for a 900 gramme sample. The formulations used were

				p.b.w.
Polyol	3000 mw			100
T.D.I.				43.7 (105 index)
Water catalyst	H ₂ O	3.5)	5.2
	Dabco	0.2)	
	L520	1.5)	
Tin Catalyst	Polyol	10)	10.3
	S _n O _c	0.25)	
	DBTL	0.05)	

It was reported that compression set figures were above average and that static flex fatigue figures were considerably improved.

The use of new moulds manufactured from a pre-impregnated sheet of phenolic resin and asbestos helped solve many of the mould manufacturing problems and many production moulds have been made from this material without undue problems.

Contd

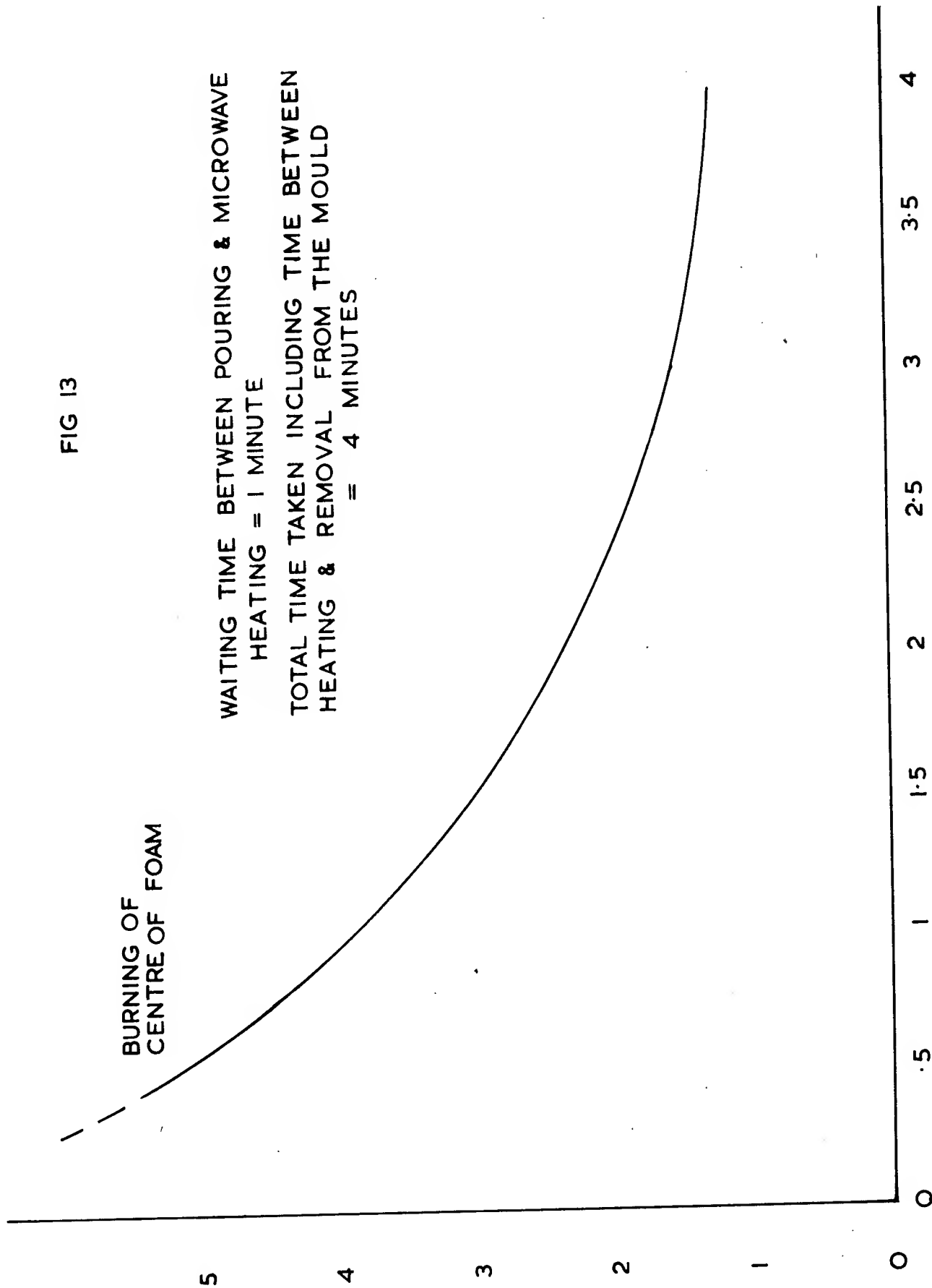
FIG 13

BURNING OF
CENTRE OF FOAM

WAITING TIME BETWEEN POURING & MICROWAVE
HEATING = 1 MINUTE
TOTAL TIME TAKEN INCLUDING TIME BETWEEN
HEATING & REMOVAL FROM THE MOULD
= 4 MINUTES

POWER
(KW)

TIME (MINUTES)



The use of new formulations resulting from very high exotherms have reduced the need for microwave heating in many cases. In spite of this the advantages that no post cure is required after microwave curing and the flexibility of operation enabling a wide range of mouldings to be manufactured with the minimum change during the production run has led to a steady demand for plants of this type.

It has been found quite easy to cure polyurethane foam mouldings which have been made with integral exterior skins. A vacuum formed ABS skin can be placed in an epoxy fibre glass mould and filled with foam. The foam can then be cured by microwaves without any problems while the ABS skin is only slightly warmed. This enables an excellent bond to be obtained between the foam and the skin but the shape and grain of the skin is retained. There is also no problem in introducing metal components into a moulding. When steel is used some heat is generated but usually only sufficient to cause a firm bond to exist between the foam and the steel. The fact that the same equipment can be used either for moulding without skins or directly into skins illustrates some of its flexibility.

For the manufacture of high density cushions it is often of interest to add a filler, the most usual being Barium Sulphate. With normal methods of heating it is found that this addition complicates very considerably the cure problem since the heat

Contd

distribution within the moulding is upset. Again using microwave energy it has been found that quite large percentages of Barium Sulphate can be added and curing carried out within the same time scale as for unloaded mouldings.

Since undoubtedly microwave energy effects cross linking by processes other than by heating it would be interesting to study the effects of this energy on other chemicals which are not now used with conventional systems. It might well be that a cheaper and yet useable chemical system could be evolved which might drastically change the economics of the process.

Fig. 14 shows a conventional microwave heating unit which is used for small scale production of flexible foam mouldings. Fig. 15., shows a mould and a typical moulding. The system shown in Fig. 14., consists of a tunnel oven supplied by a number of magnetron units some of which can be seen connected to the upper surface of the cavity. The power supply to drive the oven is shown in the cabinet. This cabinet could be situated at any convenient distance from the oven and need not be sited at the side as shown in the diagram. The equipment operates in the following manner:-

With the power off the doors are pneumatically opened and the first mould is placed in position, the door is then shut automatically and a photo cell system registers that a mould is in position and the first magnetron supplies power. After

Contd.....

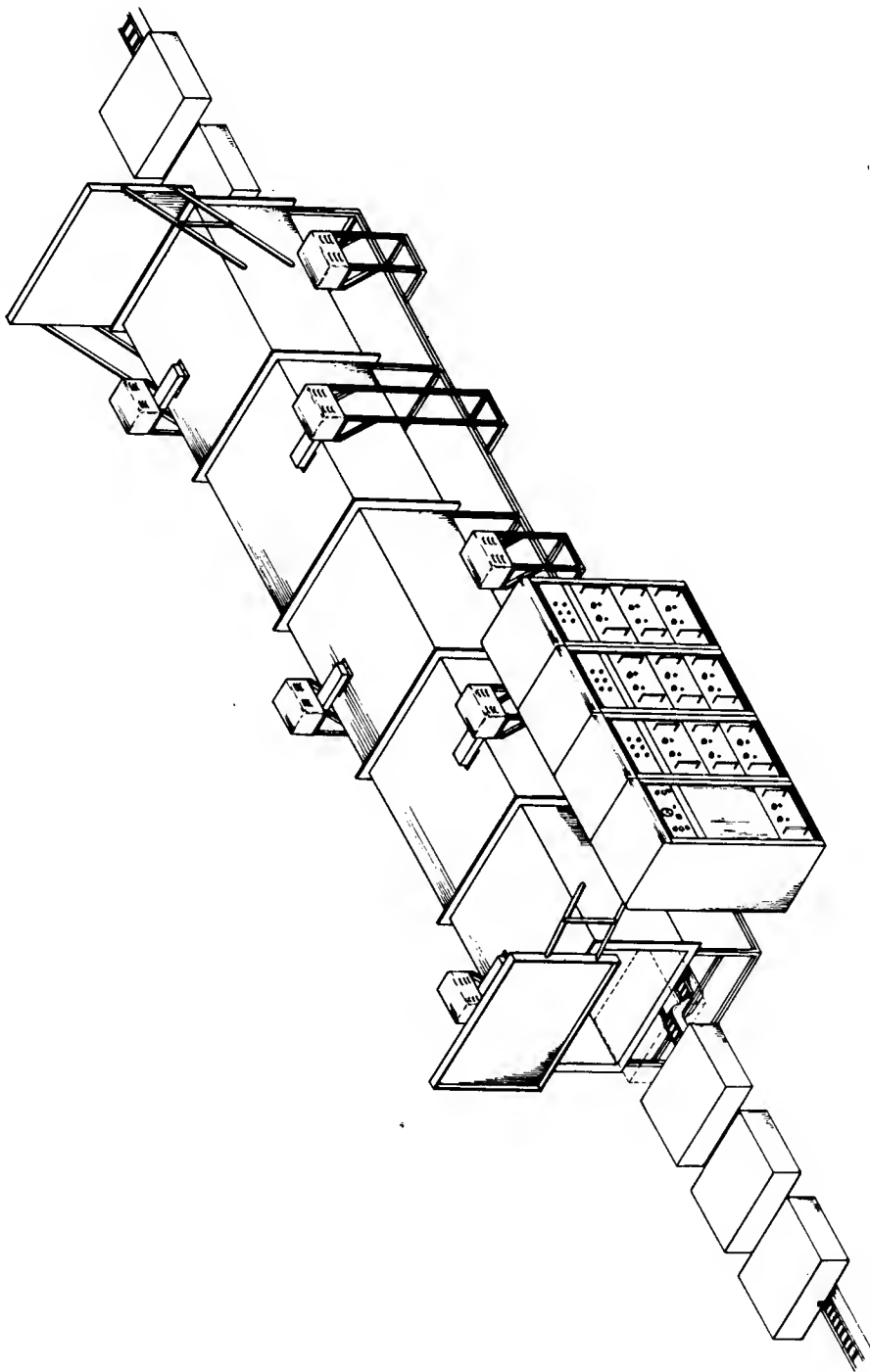


Fig.14.



Fig. 15a.



Fig. 15b.

a short interval the power is switched off, the door opened, the first mould is indexed forward and the second mould is introduced. The doors are shut and this process is repeated. This carries on until the whole cavity is loaded with moulds and all the magnetrons are working. After this one correctly processed mould is ejected from the other end of the tunnel at the same time as the new one is inserted at the entrance.

This system works very well but it suffers from the disadvantage that the power is off for a proportion of the time that the moulds are inside the cavity. This has to be so in order to allow the moulding to enter into the unit and one more moulding to be removed from the other side without power leakage. Altogether this time is of some importance and efforts have been made to find other ways and means of introducing moulds into the cavity without releasing energy.

Fig.16., shows a system which has been devised and manufactured and which works satisfactorily. The system shown is a complete curing unit intended for small scale production or laboratory use. From the plan view it may be seen that it consists of four cavities which are each supplied with magnetrons. The separation between the cavities is carried out by a system of rotating doors each with its microwave choke section. It is arranged that two ports are

Contd

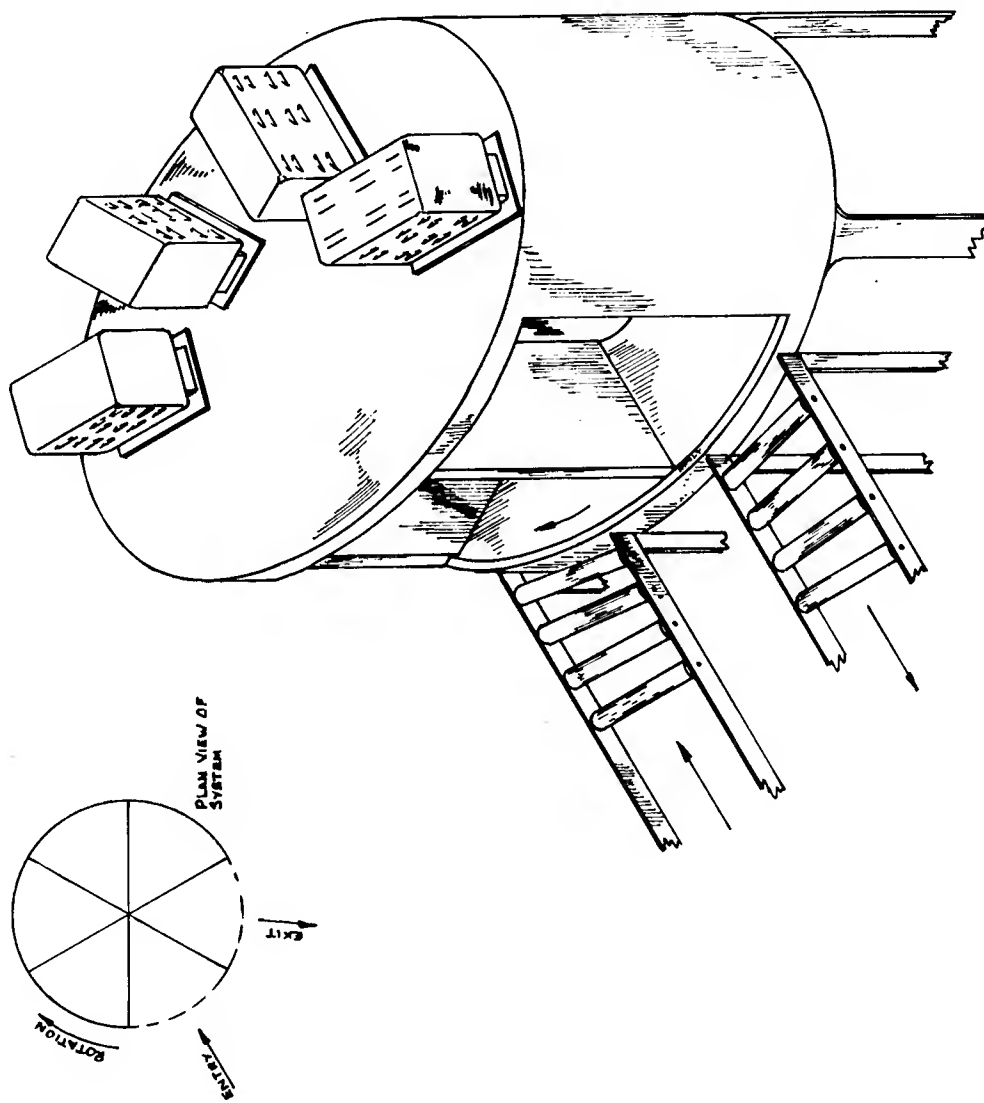


Fig. 16.

always open so that one moulding can be introduced while the second is removed. As the door system is indexed around a new mould is carried into a cavity to which energy is being supplied while the cured moulding is ejected from the other cavity. This system can easily be adapted to the entrance and exit of a large tunnel oven of the shape and size shown in Fig 14., and this completely overcomes the problem of leakage by ensuring an excellent seal at all times. The system has a further advantage that the magnetron supply need never be disconnected and therefore the total time of a number of mouldings in a cavity is much less than in the conventional system shown in Fig. 14.

Fig. 17., shows a very simple single cavity unit which has been used for pre production testing. Several magnetron units have been placed side by side to increase output but with this simple system using a single unit, five hundred seats have been produced daily for several weeks. This system for the pre production shop has many advantages, the most important being that the size and shape of the moulding can be changed easily at any time without inconvenience and excellent cures can be obtained.

Typical cure times for a 21b cushion are shown in Table I whilst Table II shows typical outputs from a microwave production equipment, the dimensions of which are shown in Fig. 18. From this data some idea of the total amount of power needed for a

Contd

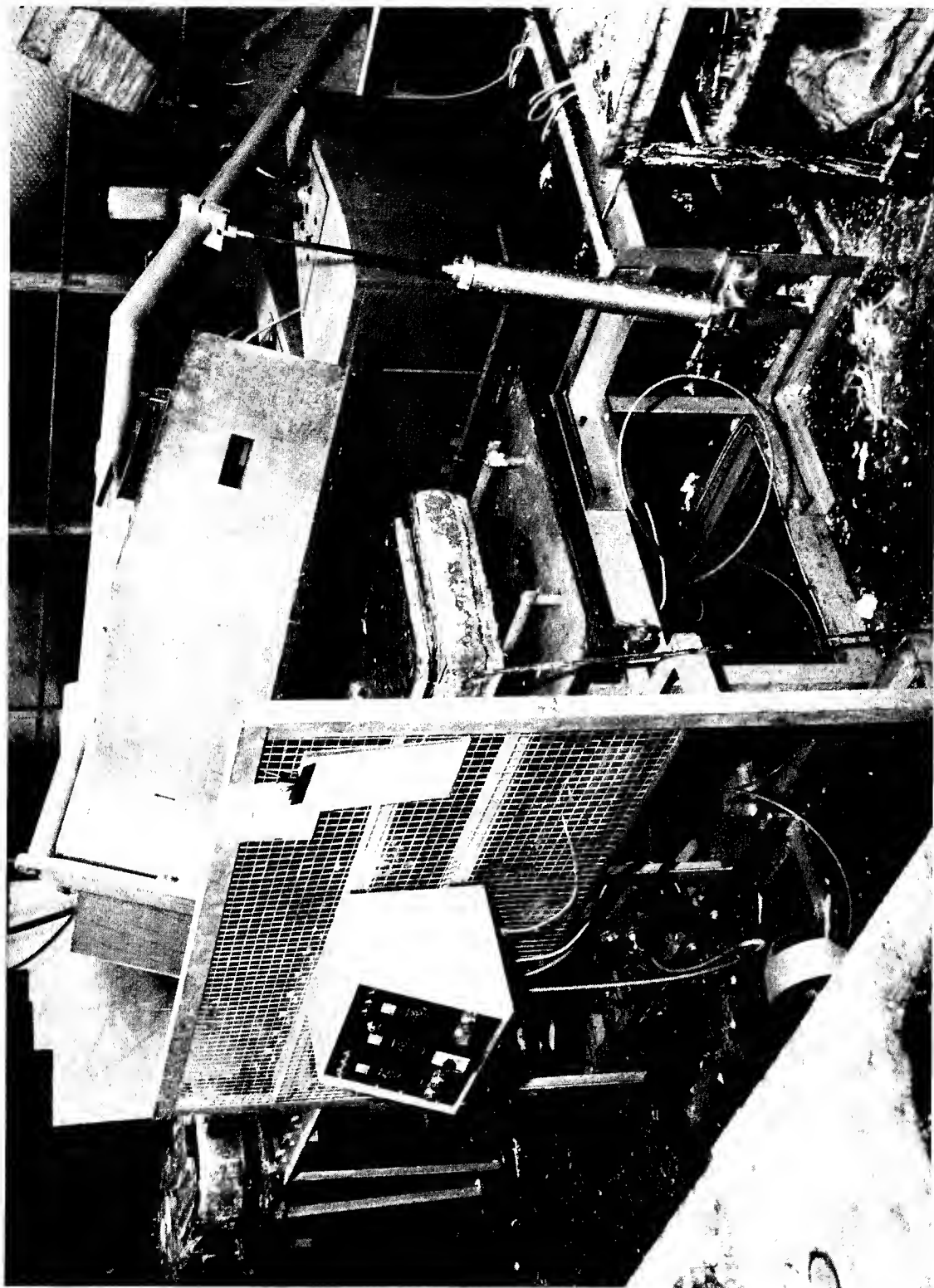


Fig. 17.

Fig. 18.

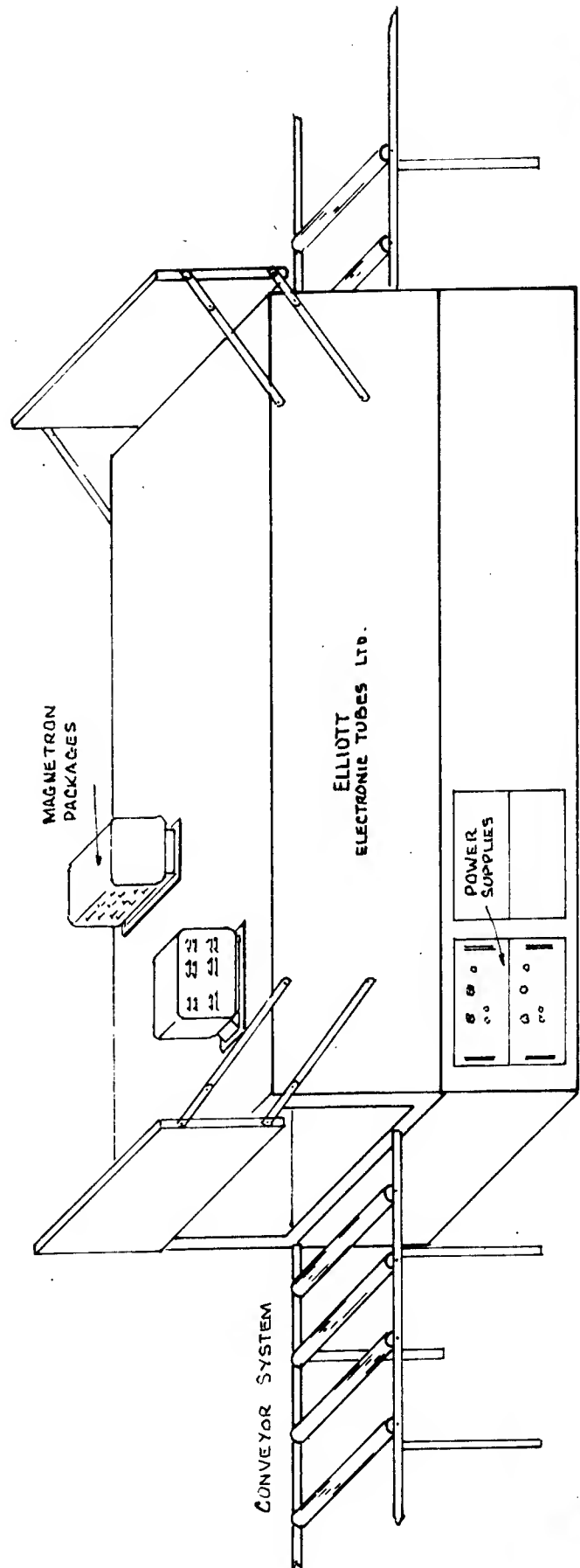
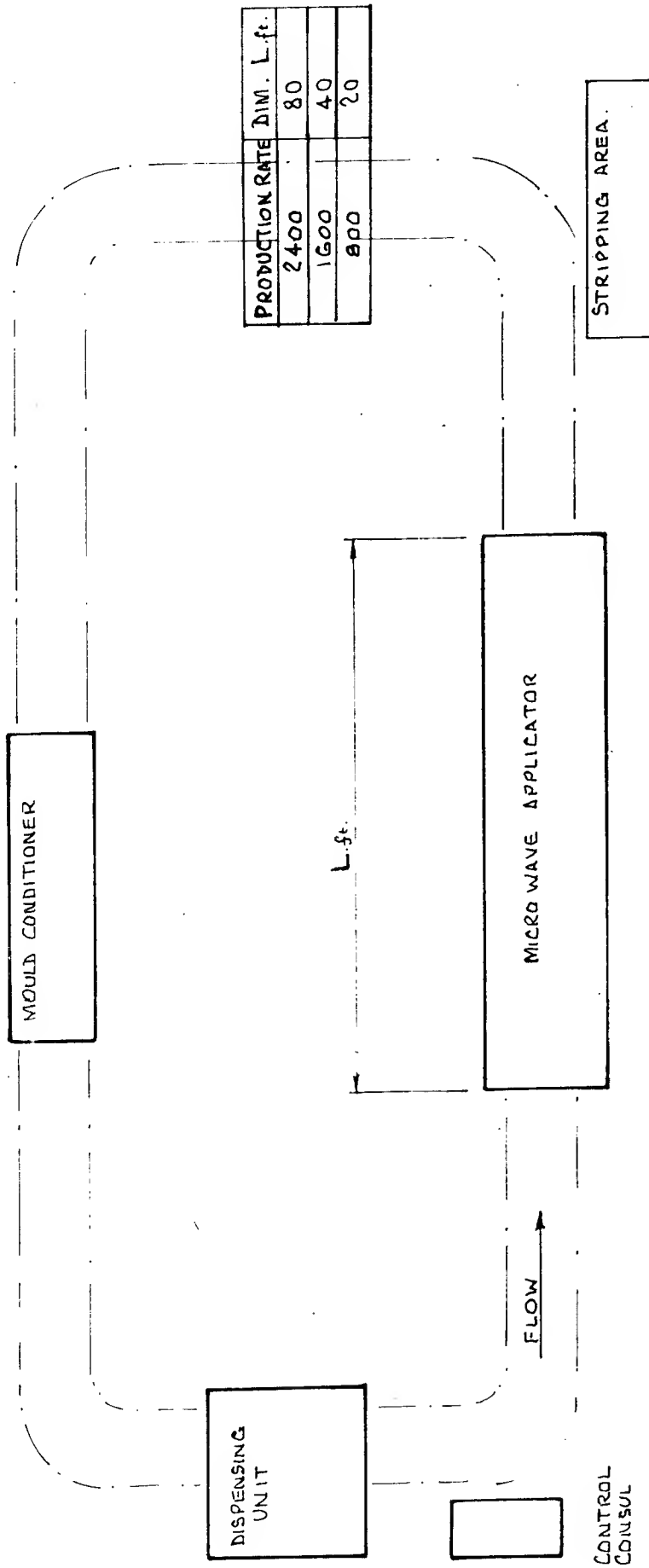


TABLE 1

TYPICAL CURE TIME FOR A 21b. CUSHION

Formulation:

			Parts by weight
Polyol	3000 Molecular weight		95
T.D.I.	80/20/Index 105		44.6
Water Catalyst	H ₂ O	3.5	5.1
	Dabco	0.1	
	Silicone Oil L520	1.0	
	N-Methyl Morphline	0.5	
Tin Catalyst	Polyol	5.0	5.3
	Stannous Octoate	0.30	
Mould Release Agent	Brulin		
Mould Temperature before filling	48-52°C		
Period held before M/W cure	120 seconds		
Microwave Power	4½ kW		
Cure Time	70 seconds		
Time before removed from mould	120 seconds		

TABLE 2

TYPICAL PRODUCTION MICROWAVE HEATING EQUIPMENT (Note 1)

Production Rate:

Moulds/8 hour shift	800	1600	2400
RF Power (Nominal)	9 kW	18 kW	27 kW
Frequency	2450 Mc/s	2450 Mc/s	2450 Mc/s
Mains Supply (Note 2) }	410-440 V	410-440 V	410-440 V
	50-60 c/s	50-60 c/s	50-60 c/s
	3 phase	3 phase	3 phase
	30 amps/phase	60 amps/phase	90 amps/phase
Water Cooling (Note 3)			
Flow Rate	12 litre/min.	24 litre/min.	36 litre/min.
Inlet Temperature	25°C maximum	25°C maximum	25°C maximum
Air Pressure	80 psi nominal	80 psi	80 psi
(Pneumatic system)	60 psi minimum	60 psi	60 psi
Main Oven Dimension	See fig. 18	See fig.18	See fig. 18

Note 1. - All data has been based on moulds weighing approximately 2 lbs.

Note 2. - Mains stabilising system can be incorporated.

Note 3. - A closed circuit water system with heat exchanger can be incorporated.

moulding line can be ascertained.

A requirement which is of some considerable importance in England is the manufacture of mouldings which use scrap foam, or foam crumb. In order to manufacture acceptable mouldings many glue systems have been proposed and tried but since the thermal conductivity of the material is very low and since most glue systems require the application of heat it is extremely difficult to apply this heat to cure the system adequately in a short time. Even though foam glues are used which can generate small amounts of exotherm it is still difficult to provide sufficient chemical energy to complete the cross linkages of this glue. Many experiments have been carried out using microwave heating and here it has been found that using a simple fibre glass mould it is easy to cure the complete moulding very quickly indeed using a wide selection of glues. From the experiments carried out to date this process does not require a release agent to be applied to the mould nor does it require heating of the mould. All the energy is absorbed by the glue and the process is extremely economical.

The use of foam backed cloth is rapidly growing and many experiments have been carried out to find a successful method of joining the cloth to the foam. Such systems in general use in Great Britain are confined to the manufacture of slab stock foam slit into layers. The layers are joined to the cloth by a

Contd

suitable adhesive. This system is quite expensive and efforts have been made to find a system which is more economic. It has been found that foam can be applied directly to the cloth and if this is then passed through a microwave cavity the foam can be completely cured quite rapidly. In this particular case the layer of foam is extremely thin and it is normally quite difficult to cure such thin layers by conventional heating without causing some deterioration of the backing fabric. With the use of microwave energy however this problem is overcome since the heat is developed almost entirely within the foam itself and good cures which ensure that the foam is firmly adherent to the cloth can be obtained rapidly.

Experiments have been carried out to determine whether or not microwave energy can be used to dry adhesives between the cloth and the foam. This has been less successful although the experiments were carried out at a time when the only known applicator was a cavity resonator. Although it is doubtful that this system would be the best for glue drying where foam is applied directly to the cloth and allowed to expand then passed into a microwave applicator, a simple cavity is still probably the best structure.

Fig. 19., shows a large cavity applicator which can be used for a system such as this in high speed production of cloth covered by polyurethane foam. It is interesting to note that

Contd

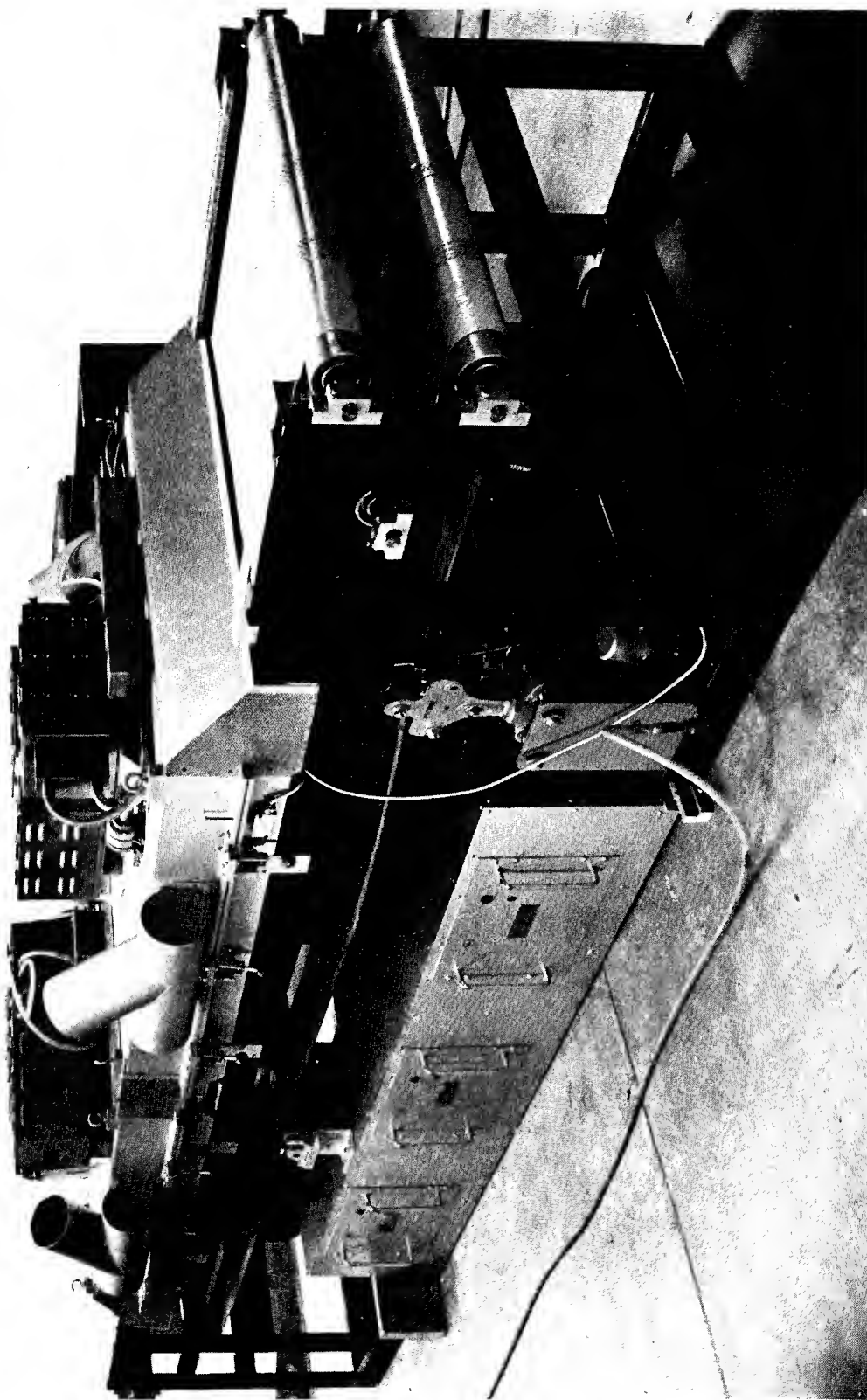


Fig. 19.

when the foam is uncured the di-electric loss is extremely high and the coupling efficiency is also high thus providing good heating until the cure is complete after which interaction between the foam and the microwave energy ceases.

It is also interesting to note that some kind of cavity resonators can be used for a wide range of objects. For instance in the manufacture of laminated rubber belting it has been found that the use of a cavity pre-heater enables output from a standard Berstof rotary curing machine to be increased by at least 40%.

So far all remarks that have been made have been concerned with the use of cavity resonators and have been restricted to flexible polyurethane foam. Before considering other types of applicators it is interesting to examine very briefly the use of microwave energy for expanding polystyrene beads and also for moulding polystyrene for which application again cavity resonators are used. Surprisingly enough the use of microwave energy for both expansion of the beads and for the production of the mouldings appears to be economic and worthwhile. The problem of expanding beads to a selected density has been overcome simply by adding a chosen quantity of water to a chosen weight of bead and placing these two components in a non lossy container within a cavity for a specific time with a known amount of power applied. The results have been the production of an acceptable quality of

Contd

bead of predetermined density. As far as moulding is concerned considerable economies can be achieved. The process is extremely simple. After expansion the beads are stored for approximately twenty four hours and then are placed in a simple wooden mould which can be airtight. Into the mould approximately 30 c.c. of water is added for each $1\frac{1}{2}$ litres of bead. The lid of the mould is closed and the unit placed in a simple cavity resonator for approximately $1\frac{1}{2}$ minutes. It has been found that initially when the mould is cold a somewhat longer time is necessary and also that it is convenient at the start of a production run to spray the mould with silicon as a release agent but using a simple mould of this kind regular spraying with a release agent is not necessary. A regular cure time of $1\frac{1}{2}$ minutes is adequate. This does seem a very simple method of manufacturing polystyrene mouldings in small quantities. Experiments have also been carried out in which other materials have been used as a mould material and production machines are now being manufactured. The advantage of this system is the extremely low cost of the mould and it seems possible to produce a moulding at least once every two minutes and possibly faster with a very simple cavity unit without the need of steam plant. The overall cost of the manufacture of small quantities of mouldings of this kind appears to be less than half that by conventional steam heating and also the reduction in complication results in a machine the actual cost of which is much less than the standard steam

Contd.....

heated machine. The considerable reduction in tooling charge for the moulds as well as the reduction of labour makes the whole unit extremely attractive. Tests which have been carried out on the mouldings made by these means indicate that they are in every way as satisfactory as mouldings carried out by conventional heating systems.

Some considerable attention has been paid to the possible use of microwave energy for curing rigid polyurethane foam. In particular when this is used for the manufacture of laminated building board it often becomes difficult to cure. In this case the application of microwave energy must be restricted to a system where one or other side consists of a material which is transparent to microwave energy. Systems which have been tried use hard board and on occasions Plaster-of-Paris. Microwaves have been used successfully with both types of material.

The mechanical feeding system for the boards has produced many problems and many types of microwave applicators have been proposed. However one system in use consists merely of a microwave cavity through which the sandwich feeds. The lower board of the sandwich is sprayed with foam which is allowed to expand after which the top board is placed in position and the whole assembly is passed through the cavity resonator. The heat generated by interaction of the microwave energy with the foam is sufficient to cause cures in close proximity to the boards

Contd.

and results in a good bond between the foam and the board. From present experimental evidence it would appear that a second method is capable of working quite well and this does not involve heating the foam but merely on heating the surface of the board before foaming. The surface of the second board is then heated before it is placed on top of the foam after the foam has risen. The heat contained within the board together with the exothermic reaction results in a complete cure of the foam in close proximity to the board and also in a good bond between the foam and the board. This system offers some considerable advantages since the microwave unit is only concerned with warming the surface of the board and for this system applicators other than cavity resonators can be used with some considerable advantage.

There are two types of applicators which are of general interest other than cavity resonators. The first is the karp structure. The karp structure is a microwave structure which was developed for use with high power travelling wave tubes to enable good interaction to be obtained between the electro magnetic field and the electron beam. Fig. 20., shows a diagrammatic representation of this kind of slow wave structure. This structure when carefully designed has rather unusual properties since the electro magnetic radiation from the surface falls off very rapidly, as a result of which although not shielded no field exists a short distance away

contd

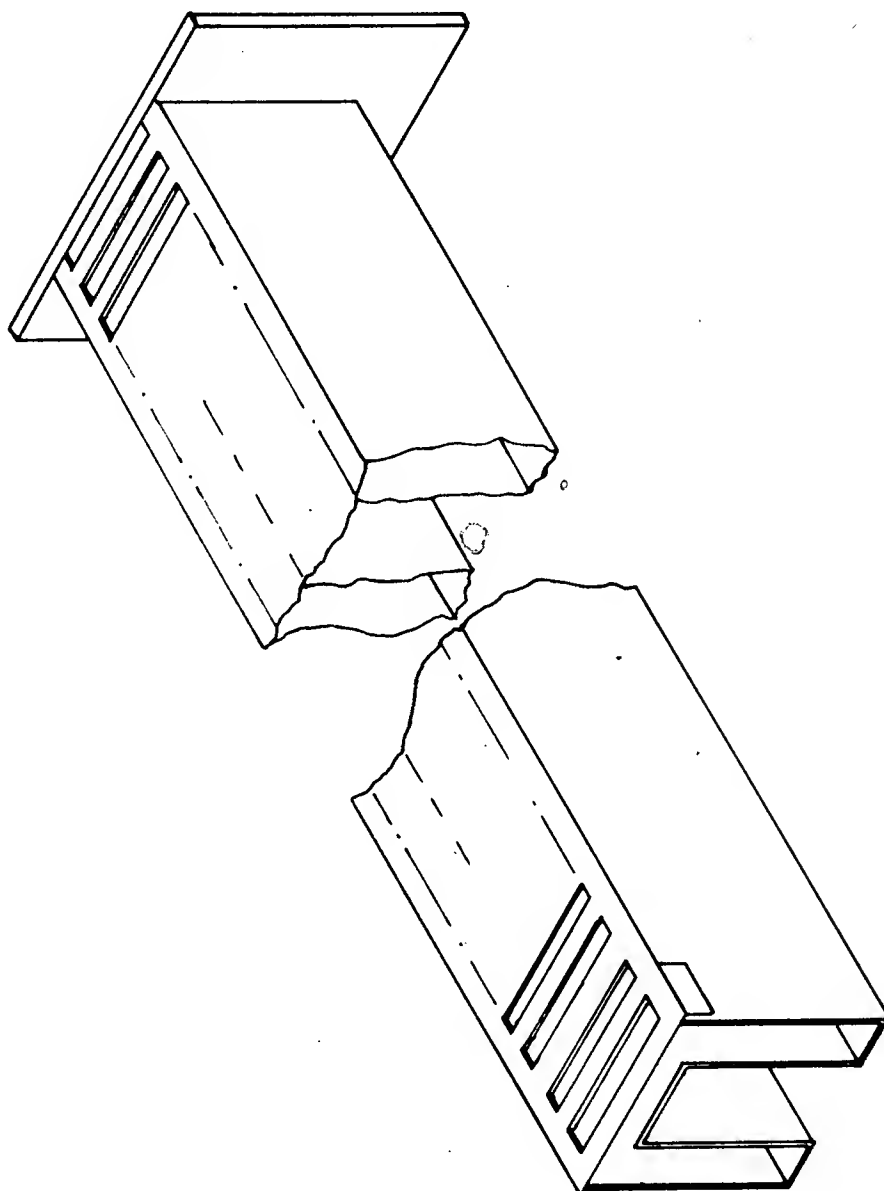


Fig. 20.

from the radiator surface. If therefore a structure of this kind is placed near a lossy material such as a building board the energy will couple to the building board but will not couple to any material placed a short distance away. For the kind of application described above it is therefore convenient to have a small battery of karp structures fed by microwave energy over which the building board passes. The microwave energy reacts with the building board and causes the surface to heat rapidly. The building board can then pass underneath the foaming machine and a second board pass over a second system of karp structures. As soon as the foam has risen the second board is placed on top of the foam and the system is complete. This microwave system is extremely convenient as the energy is applied to the board from one side only and yet is completely safe. The karp structure was originally developed for use with microwave heating when the need arose for drying PVC adhesive when used in book binding. In this particular case the spine of the book is coated with PVC adhesive which is then partially dried by passage over one karp unit. The covers of the book are then put into place and the whole passed over a second karp structure which completely dries the glue and enables the operator to take the book and to cut the pages immediately. This process obviates the use of hot set glues which are complicated and expensive or long delays which necessitate large storage spaces.

In addition to the karp structure the simple helix which

Contd

is also a slow wave structure used in the manufacture of travelling wave tubes has been found of considerable interest and use for applying microwave energy. Fig. 21., shows a simple helix arrangement which has been used for high speed curing of rubber extrusions and the addition of a simple unit such as this to the end of an extruder has resulted in large solid sections being vulcanised in very short times without the necessity of a salt bath. Where production has to be speeded up such a unit placed between the extruder and salt bath has enabled the extrusion speeds to be increased considerably. As far as cellular plastics are concerned however the helix has been used for curing polyurethane foam which has been injected into PVC tubing. This particular case is of interest because the volume of the foam is so small that adequate generation of heat by chemical reaction is not possible. The use of microwaves in this form enables efficient coupling into the foam and curing is rapid and complete. It has the advantage that all the heat energy is contained within the PVC skin and no damage occurs to the PVC by this process. Fig. 22., shows a simple experimental unit which has been used for trials. This applicator design gives maximum utilisation of the available microwave power which is concentrated into a very short space and enables a high rate of heating to be achieved. A variable speed conveyor belt is provided to carry the section through the device and the microwave

Contd

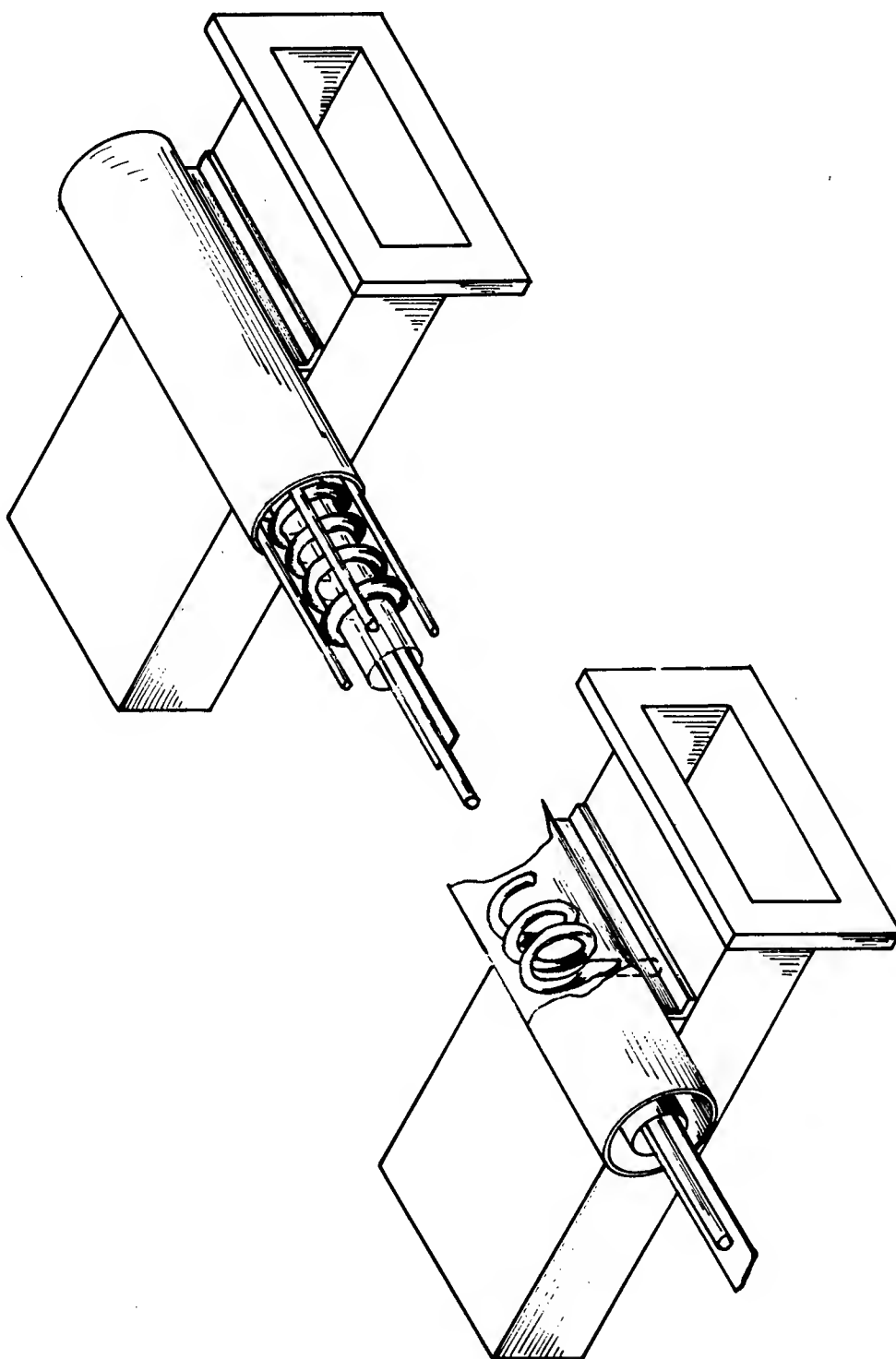


Fig. 21.

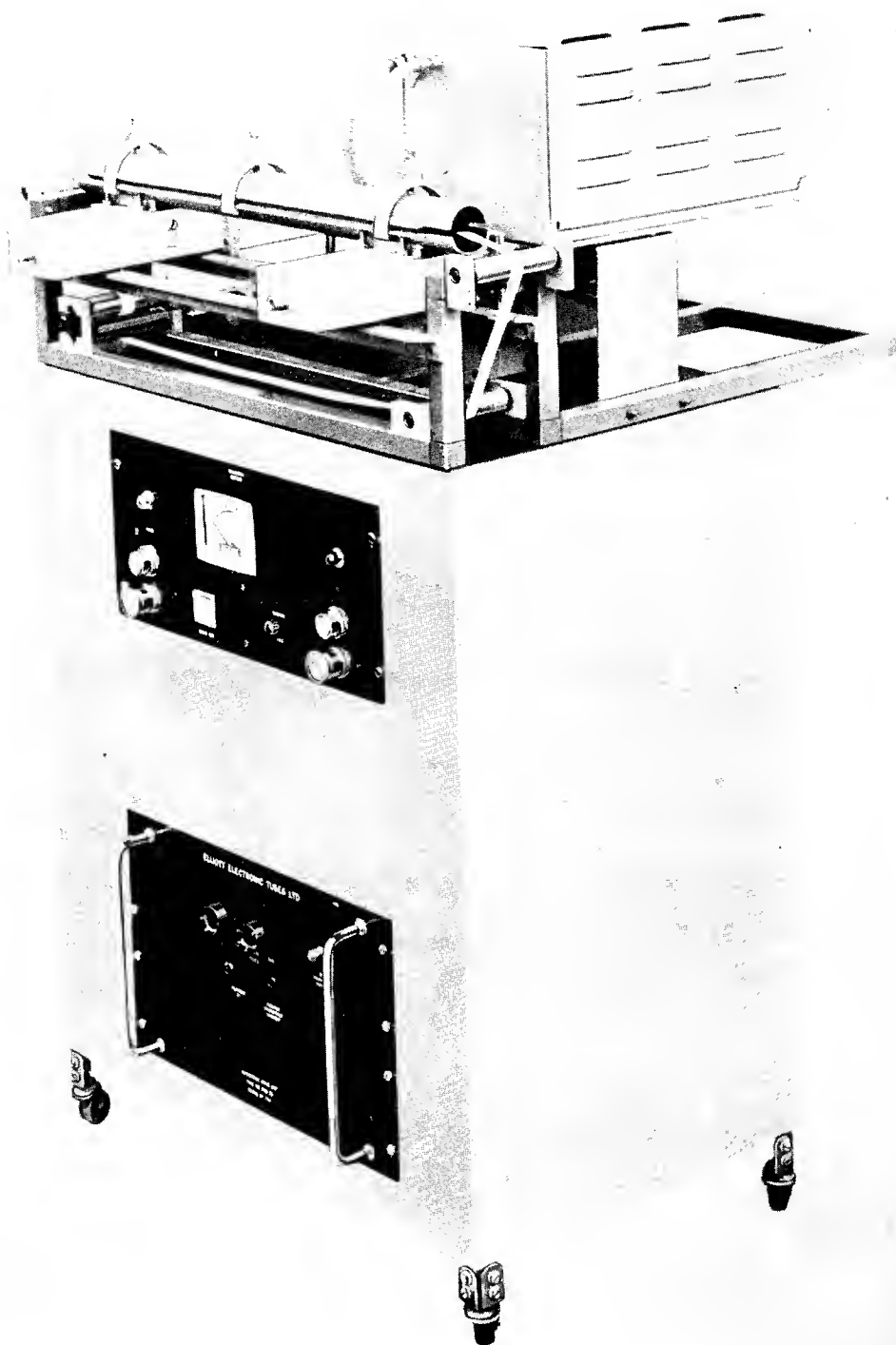


Fig. 22.

power level can be adjusted to suit the material, size of the section and the rate of production. This equipment can be adapted for any factory use varying from a simple self-contained system to a complex array of applicators powered from a central control console for mass production.

Costs.

The only reasons for introducing microwave heating into any system must be either reduction in costs or improvement in quality. The cost reduction can be reduction of capital equipment costs or running costs. In certain circumstances it has been found possible to change the processing schedule so that even though the heating is more expensive using microwaves there is ultimately a reduction in the total cost of the whole process.

At the present time all installations have been made with either $1\frac{1}{2}$ or $2\frac{1}{2}$ Kw magnetron units. This has been done on the basis that it is cheaper to manufacture large quantities of small units than it is to manufacture single units of high power to fit a specific requirement. At the present moment it is not easy to obtain very high power magnetrons at a low price also because the costs of magnetron manufacture are critically dependent upon the number of tubes being manufactured and although in the future one can foresee a system where magnetrons of 10 and possibly 25Kw will be employed this can only occur when the requirement for such high powers enables the magnetron tube manufacturer to set up to manufacture reasonable numbers. At the present moment

Contd

therefore all considerations of costs are related to multiple units of rather low power magnetrons coupled to one or more applicators.

As far as the experiments we have carried out and also as far as the major production installations we have made, are concerned we have found multiple units of $1\frac{1}{2}$ to 2Kw quite satisfactory. The cost of such a tube is in the neighbourhood of £120 and at the moment we are finding that the average life is in excess of 7,000 hours. With such cheap tubes and such long lives the replacement magnetron cost when considered in relation to the electrical consumption is not very significant.

With regard to the efficiency of the installation, the efficiency of conversion from mains electrical energy into microwave power output is in the order of 70% and the conversion of this power into heat within the object to be heated is critically dependent on the di-electric loss of the material to be heated and its coupling to the applicator. It is possible under certain favourable circumstances to obtain 90% efficiency. On the other hand where it is not easy to match the load to the generator the coupling may be as low as 50%. The total efficiency of the system from energy supplied by the mains to energy turned into heat within the material itself can vary from 35% in the worst case to something like 68% in the best case.

Contd

The fact that electrical energy has to be used may mean that the system cannot compete economically with cheap process steam. On the other hand where steam raising plant is not generally available the high efficiency of energy transformation may well render the whole process economic.

The cost of the capital equipment is of course dependent on the power. The cost of each module is constant but the cost of the applicator varies with the power required and the cost of the control unit varies with the complexity of the operation. For installations of over 10Kw it is convenient to remember that the capital cost of the equipment is usually of the order of £1,500 per Kw. These figures are based on the manufacture of a single unit to suit the individual customer's requirements and even a moderate quantity production run of any unit can show dramatic savings.

The use of frequencies other than 2,450 mc/s is limited also by the availability of magnetrons and their cost. Although in certain circumstances high frequencies would undoubtedly be useful, particularly in certain glue drying operations the cost of manufacturing magnetrons in small quantities with high power output at this frequency precludes their use for industrial operation. It is also very important that the life of the tube should be adequate and as a guide to the ultimate life that a tube should have,

Contd

we believe that the replacement cost for the tube should never be greater than the cost of the amount of electricity used during the tube's life.

It can be seen that from the figures quoted the magnetrons that have been used to date have much better lives than this figure calls for and in general are quite satisfactory. This would not be the case with high frequency tubes.

Future Applications.

The amount of experimental work that has to be carried out in order to determine whether or not a process can be adapted to the use of microwave energy is considerable. Because of this and the difficulty in the early stages of assessing the probable financial benefits which can be obtained from such processes, the applications of this form of heating energy are being introduced extremely slowly. Nevertheless in the cellular plastic field there would appear to be great opportunities in the future especially if one takes into consideration the particular advantages of the use of microwave energy, such as the fact that irregularly shaped objects can be heated quite uniformly provided that they have high di-electric loss, and that the thermal conductivity of the material is of no importance. It is thus possible to heat materials which otherwise cannot easily be heated, at quite high speed.

Contd

From the work that has been carried out to date it also seems possible that the use of microwave energy for initiating chemical reactions has possibilities. Little or no work has been done in this field although experiments are now in hand to discover the effects of this energy in initiating chemical reactions. It is believed that many chemical processes can be cheapened by the use of this method.

A considerable amount of work is being carried out and experience is being gained in the field of industrial microwave applications both for heating and measurements and so far results are extremely encouraging.

*

L. Absil. Le préchauffage des Matières Thermodurcissables par pertes diélectriques on préchauffage H.F.
Revue Belge des Matières Plastiques No. 4. 1963
Page. 283-294.

M A R K E T S A N D E C O N O M I C S O F
C E L L U L A R P L A S T I C S

ENGINEERING SUMMER CONFERENCES

WAYNE STATE UNIVERSITY

MAY 5, 1967

RAYMOND L. SIREN
MOBAY CHEMICAL COMPANY
PITTSBURGH, PENNSYLVANIA

MARKETS AND ECONOMICS OF CELLULAR PLASTICS

I INTRODUCTION

May I first take this opportunity to thank Wayne State University for inviting me to participate in this Engineering Summer Conference. From what I've seen and heard this week, this conference is extremely worthwhile and most successful in fulfilling its difficult task of summarizing the chemistry and technology of the foam plastics. I can only hope that my treatment of the subject of marketing factors is as comprehensive and useful to you as I'm sure the rest of this conference has been.

* * *

Before taking up the topic of "Markets and Economics of Cellular Plastics," I'd like to preface my remarks with an acknowledgment of bias and a general disclaimer.

As I'm sure you know by now, my employer, Mobay Chemical Company, is involved in the production of raw materials for only one of the cellular plastics we've been discussing this week--the polyurethanes. Consequently, my objectivity is admittedly somewhat less than pure.

However, I have been fortunate in gaining the cooperation of several market researchers in other companies involved in other cellular plastics and the data presented here reflects that cooperation.

Furthermore, while a bias in the direction of one's own company's products is natural, objectivity with regard to competitive products is a fundamental requirement for successful marketing research. I trust this paper reflects adequate objectivity.

Also, in order to present a meaningful discussion of economics, it is necessary to use price and cost figures--in this case, for products which my company does not make. Any such figures you hear are therefore to be considered as approximations and I ask you not to quote me under any circumstances without specific permission. My remarks today are made in an effort to bring commercial perspective to the technology you have heard and no endorsement of the marketing and economic information contained in my talk is either expressed or implied by Mobay. Thank you for your cooperation.

II MARKETS

Now then, let us take up the subject of the markets for cellular plastics.

A great number of market researchers have published reviews or surveys of foam plastics markets. Several of these are noted in the bibliography. Agreement among these several published reviews is rare. Even rarer is agreement insofar as forecasted future markets are concerned. This is entirely natural as several different commercial points of view are involved.

The problem, however, lies in the fallacious elevation of a forecast to the status of a prophecy--as if the market researcher had the mystical ability to foretell the future. This, of course, is absurd.

The estimates of future markets we will discuss today are not to be construed as prophetic, but rather as statements of potentials--if, and I emphasize that big if, certain qualifying requirements are met. Consequently, in many cases, we will consider a range of numbers when defining markets; and the width of that range is in part a measure of the magnitude of the "if" involved.

In other words, we will consider first, the total market potential, and then by examining the problems that must be solved, get some idea of the markets that may in fact result.

FLEXIBLE FOAMS

The largest market today for cellular plastics is flexible foams. It is a market dominated by the flexible urethanes and the rubber latices.

It is also a market that can be considered relatively mature--that is, one where the pattern of growth has leveled off to a rate only slightly in excess of that of the growth of the chemical industry as a whole.

Table I describes the markets for flexible foams and provides an estimate of the materials involved.

Historically, this market has seen the growth of flexible urethanes from approximately 19-20 million pounds in 1957 to the levels shown in Table I. Accompanying this growth in urethane sales has been a decline in foam latex participation from

2-A

TABLE I

FLEXIBLE CELLULAR MATERIALS

(millions of pounds)

<u>MARKET CATEGORY</u>	<u>1962</u>	<u>1966</u>	<u>1970</u>
FURNITURE	150	200	230-310
TRANSPORTATION	65	140	190-340
BEDDING	45	60	65-110
TEXTILES	10	47	60- 75
MISCELLANEOUS	<u>30</u>	<u>48</u>	<u>55- 85</u>
TOTAL	300	390 495	600-920

<u>MATERIAL</u>	<u>1962</u>	<u>1966</u>	<u>1970</u>
URETHANE	145	320	440-650
VINYL, OTHERS	35	50	60-100
LATEX	<u>120</u>	<u>125</u>	<u>100-170</u>
TOTAL	300	495	600-920

of (p. 2) - also, in table

1962-1966

1967-1970

approximately 210 million pounds in 1955 to a bottom of about 120 million pounds in 1962. As you will note from the table, this is expected to be the low point, and foam latex can be expected to "fight back" to possibly 150 million pounds in the late sixties.

Along with the decline in latex sales, there has been a shift in the chemical makeup of latex foam. For instance, in 1958, almost two-thirds of the latex total was of natural rubber origin. By 1968, however, natural rubber will be only about 20% and the major foam latex material will be SBR or butadiene-styrene derived.

Because of certain unique properties, vinyl and polyethylene foams will hold about 10% of the total market. This is due largely to their closed cell structure and will largely be in certain specialty furniture, gasketing and padding applications.

In general, the rise in urethane foam participation can be traced to its favorable price structure coupled with satisfactory physical properties and ease of fabrication. Originally regarded as chiefly a high quality foam for the high quality markets, the urethanes are now used as industry work-horses--in Chevis as well as Rolls-Royces.

* * *

A few comments about the individual markets may be in order.

Furniture

This market is generally characterized by 5 to 10 major furniture companies that tend to dominate production techniques and styling, and lead the balance of the industry toward new developments. Furniture industry leaders are constantly looking for new manufacturing techniques as a means of increasing profits. Urethane foam offers several such possibilities--for instance, the technique of foaming frame and cushion in place--thereby decreasing hand labor.

It should be pointed out that in past years, the major furniture usage of urethane foam has been on a replacement basis. The development of new fabrication techniques and molding methods has enabled the furniture industry to regard urethane foam as a raw material in its own right and the markets have responded accordingly.

There is a pronounced trend, in this and the automotive market, in the direction of molding foam products as opposed to cutting cushioning from slabs. As this trend and its underlying technological forces increase, there is every reason to expect more captive manufacture of foam products by the original equipment manufacturers.

Transportation

Urethane foam is finding rapidly growing acceptance in passenger vehicles which is the volume portion of the transportation market. Although aircraft and commercial transportation seating is perhaps more widely publicized, the great majority of foams for this market go into the passenger automobile.

Automotive safety is currently the subject of intense investigation by both government and industry, due largely to the notoriety generated by the book "Unsafe at Any Speed" by Ralph Nader. This attention and the desire of automobile manufacturers to police themselves rather than be burdened with government-enforced safety regulations has caused a sharp upturn in the usage of semi-flexible foam in safety padding.

The amount of foam used in an automobile, therefore, includes not only that required for seating, but a host of smaller parts including headliners, crash pads, sun visor padding, arm rests, carpet underlay, gasketing, window harness, thermal and sound insulation and carburetor air filters.

Here again, new technology of molding has encouraged greater use through labor cost reduction.

Mattresses and Bedding

Among the major flexible foam markets, it is perhaps here that the competition is keenest.

This market is made up of three structural levels; the first and dominant level consists of two nationally organized companies and two so-called franchise houses, a second level consisting of a number of moderately sized firms, and a third level characterized by small local neighborhood producers.

Depending upon the company and their degree of internal integration, the market can be divided into two categories: foam cores and foam pads in conjunction with springs. Those manufacturers basic in spring manufacture are reluctant to convert to full foam

mattresses and this has been a major deterrent to foam usage. They are being aided by heavy promotional efforts on the part of the spring steel industry.

To counter this deterrent, there is a trend on the part of foam producers to enter the mattress business.

As an outgrowth of the intense competition, the National Better Business Bureau last year released its Service Bulletin Periodical No. 1879 which recommends that "in all advertising and labeling of 'foam' products, the type of 'foam' be affirmatively and conspicuously disclosed in immediate conjunction with the term 'foam' wherever used." Unfortunately, this recommendation has been widely interpreted to mean that the word "foam" should only be used to describe a rubber product. Regrettably, the NBBB has yet to make its viewpoint clear and considerable competitive confusion exists.

The Flexible Foam Producers Committee of the SPI Cellular Plastics Division has initiated projects which promise to increase the vigor of urethane foam competitive activity. One of them is the establishment of a "Seal of Quality," which is intended to instill confidence by the consumer in the quality of the foam he is purchasing.

Another project is an outgrowth of the finding of Charles Lappen, Marketing Consultant, who was retained by the Committee to investigate the bedding market and recommend a program of industry wide promotion of urethane foam bedding. The Lappen report points out that the long range growth trend of bedding industry sales is from \$470 million in 1965 to \$835 million in 1975. It further points out that urethane foam is presently inadequately represented in manufacturer's product lines and an intense promotional effort is necessary to assure participation in this growth.

Clothing Interlining

The garment interliner market became a significant market for urethane foam by virtue of an explosive growth in 1961. As anyone who follows the changing hemlines of milady's skirt will surely know, this industry is subject to fashion fads. It was largely due to such a fad that the interliner market was created.

However, as the usage of urethane foams is now well entrenched, particularly in outerwear and juvenile garments, and because

there are a number of other garment industry uses besides interlining (intersoles for shoes, handbag lining, accessories, etc.) a steadily growing penetration is assured.

Structurally, this market is made up of a host of small fabricators and jobbers, but there has been a distinct trend toward integration by the textile industry backwards into foams and by the foam producers forward into textile laminating.

It is interesting to note that while polyether foams have generally taken over the flexible markets due to lower costs, the polyester formulations have managed to hang on to a large part of this market because of their ability to be flame-laminated and primarily because of their solvent resistance.

Other Markets

Packaging, of course, is a most cost-conscious market, and will be discussed again under rigid foams. It can be noted here, however, that this market provides a convenient outlet for some of the scrap produced in foam fabrication.

Carpet underlay have been slow developing, largely due to a lack of the intense marketing effort displayed elsewhere. Since the other markets have now been well penetrated, the rug underlay market should begin to rise sharply as industry promotion is focused on it. Recent technological and fabricating advances in the area of foam-backed carpeting will help boost the market growth.

The miscellaneous markets, among which may well be found a future major market, as development and marketing efforts are increased, include:

- Shredded fill for toys
- Seals, gasketing and channeling
- Hair curlers
- Sponges and household novelties
- Air filters
- Accoustical wall and ceiling tile
- Rail car journal box lubricators
- Sporting goods padding
- Daubers and application novelties

While I appreciate that the foregoing discussion of flexible foam markets has been perhaps overly brief, I trust you will grant me the privilege of passing over to consideration of the rigid foams for a number of reasons:

- (1) Marketing and R & D emphasis is switching towards rigids.
- (2) The markets are more diverse with more intense intramural competition among cellular plastics.
- (3) Growth rates and future potentials exceed those of the flexibles.
- (4) I think they are more interesting to study.

RIGID FOAMS

Any attempt to consider the markets and the economics of rigid foams separately is a lot like the classic debate: "Which came first, the chicken or the egg?" However, I think we can manage a reasonably clear examination of the rigids by considering first the markets and potentials, and then investigate the economics that are responsible for these markets. Bear with me because there will have to be some jumping back and forth.

The relatively recent commercial history of rigid foams has been characterized by fairly rapid growth and the frequent initiation of totally new, very attractive market areas. This has led to a proliferation of market forecasts that often border on astronomical in their statements of markets a few years hence. However, the market growth, rapid as it may be, is only now beginning to show positive signs of approaching the large volumes these forecasts indicate. We hope today to analyze this market situation and discuss the key areas where breakthroughs are needed.

Current and forecasted markets for rigid foams are outlined in Table II.

In probably 90% of this market, rigid foams are used because of their thermal insulation properties; (the exceptions being mostly marine flotation and some aspects of packaging). If future markets are to be based on insulation alone, perhaps the market will double in five years, but there is probably a limit--perhaps 315 million pounds--to the market potential of these high efficiency, relatively expensive insulants.

Possibly this forecast can be regarded as just another pipe-dream, no different from the many optimistic estimates that abound in the trade literature. However, it is felt that the higher numbers in the ranges cited can be reached if certain provisions are met. Table III lists several basic requirements that qualify the higher values in the forecast.

Let us review each of these qualifying requirements.

1. Resolution of the problems of Building Codes and Product Approvals

The problem here is two-fold. The further development of better fire resistant foams must proceed, and indeed is probably the major item in the R & D programs of foam producers. Some foams satisfactory for code and insurance approval now exist, but a great number of foams sold and advertised as S.E. are far from passing the required tests for approval.

The second problem is perhaps more critical--that of gaining code acceptance of the fire retardant foam if and when developed. The code/insurance authorities tend to follow outdated if not archaic procedures. One needs only to consider the fact that millions of units of highly combustible materials--wood, paints, etc.--are perfectly acceptable today, and the conclusion has to be drawn that this is not as much a problem of technology as it is one of bureaucracy, politics, lack of organization, etc.

The solution of this latter problem is probably best found in an industry-wide, organized approach and the SPI is taking several positive steps in this direction with its Code Advisory Committee activities and its Plastics in Construction Council.

2. Economic factors

The next four qualifications all come more or less under the general heading of economic factors, but represent four fairly distinct problem areas.

(A) Usage of foams as more than insulants, that is, as structural components and for fastening and fabricating purposes.

The sale of rigid foams strictly on the basis of their insulating efficiency is a marginal prospect at best. Furthermore, it is wasteful in that it neglects the fact that the rigid cellular plastics offer significant structural value when used in a properly designed structure.

TABLE II
RIGID CELLULAR PLASTICS
(millions of pounds)

<u>MARKET CATEGORY</u>	<u>1962</u>	<u>1966</u>	<u>1970</u>
CONSTRUCTION	30	80	170-245
TRANSPORTATION	10	36	65- 90
APPLIANCES	15	33	55- 90
MARINE	10	27	45- 75
PACKAGING, CUPS	25	63	100-200
MISCELLANEOUS	<u>15</u>	<u>44</u>	<u>45- 55</u>
TOTAL	105	283	480-755

<u>MATERIAL</u>	<u>1962</u>	<u>1966</u>	<u>1970</u>
URETHANE	22	110	200-500
POLYSTYRENE	78	163	250-300
OTHERS	<u>5</u>	<u>10</u>	<u>30</u>
TOTAL	105	283	480-755

TABLE III
QUALIFYING REQUIREMENTS
FOR
HIGHER FORECAST

1. Resolution of the problems of Building Codes and Product Approvals.
2. Economic Factors:
 - A. Usage of foams as more than insulants, that is, as structural components and for fastening and fabricating.
 - B. Development of better installation and fabrication techniques.
 - C. Establishment of wider ranging distribution channels.
 - D. Board foot cost (in place) competitive with or better than other materials, based on price-property considerations.

The sandwich panel, described earlier in this course, using rigid foam as a core between thin, higher strength facings, provides a means whereby a designer can achieve the most strength out of the least amount of material. Sophistication in the use of the sandwich concept is lacking in this country, while in Europe, more attention is being given to the properties of material combinations. Progress is being made, however, and more industry attention is being focused on this developing technology.

The conventional practice is to use foam strictly for insulation, and to get all the necessary structural strength from the facing materials. This is expensive--largely because facing materials are expensive on a strength-weight-cost per unit volume basis.

There are, however, a growing number of examples where enlightened researchers are investigating the usage of material combinations.

(B) Development of better installation and fabrication technique.

The development of rigid foam chemistry and materials technology is far ahead of the development of techniques for using foams. In many respects, we are trying to use the cellular plastics in the same manner as has traditionally been used for conventional materials such as fibrous glass and the inorganic insulants, and have neglected to develop new fabricating procedures for which the foam plastics seem better suited.

A lot of discussion is given the ability of the urethanes to be "foamed-in-place" but I truly question whether we have really begun to utilize the full potential of that unique property.

Techniques must be found and developed that permit the use of foams not only as insulants, but also as structural members, fastening media, coating and corrosion prevention materials, and in general, as a means of reducing overall fabricating costs.

(C) Establishment of wider-ranging distribution channels.

Of course, solution of this requirement will at least in part be a natural consequence of the increasing demand for foams. However, we in the raw material supply business are well advised to do all we can to encourage the entry into the market of new systems suppliers, foam producers, applicators, contractors, etc.

It seems apparent that there is a big gap in the distribution scheme today--between the abundance of raw material sources and the blossoming demand at the consumer level. This gap is in the lack of distribution centers, system suppliers, retail outlets, foam applicators, machinery suppliers, etc. The good word must be spread to the retail lumber and building materials dealers, furnace and insulating contractors, real estate developers, pre-fab house manufacturers and the like.

(D) Board foot cost (in-place) competitive with or better than other competing materials, based on price-property considerations.

This, of course, is the major requirement. And, I think we're winning the battle with our competition. As sales volumes increase, it is quite natural to expect prices to come down--this has happened in the past and the downward trend is still with us. As an example of the trend toward lower prices, the price of TDI, the major urethane raw material, has dropped over 50% within the last three years.

In addition, there has been and will continue to be research into lower cost urethane foam systems. Some of this has already been published, notably the work with crude tall oil and forest product material extended foams.

Strangely enough, even with some of this work already done and published, little commercial usage has been given such foams.

* * *

Having reviewed the size of the potential markets and the necessary conditions for achieving these markets, we can now consider the individual market categories.

Construction

This market, the largest today, represents approximately a little less than half of the total potential market. And of this total, residential housing usage is potentially half. Thus, the usage of foams for residential building is the largest single market category.

Of course, building codes and product approvals present a major problem, but it is noteworthy that in the residential building instance, the problem of building codes, etc., is not nearly as severe. Combustible materials have long been used in housing

construction--chiefly lumber. Therefore, if diligently pursued, acceptance of the cellular plastics by such agencies as the code groups and FHA should proceed readily.

The biggest deterrent to residential use is probably more one of architecture and esthetics than it is of codes. The attempts by the plastics industry to sell their wares by combining the new materials of construction with a new method of construction have been singularly unsuccessful. The several all-plastic "houses of tomorrow" scattered here and there around the country are usually described as "nice places to visit, but I wouldn't want to live in one."

Here, we are somewhat at odds with the architects who envision a new architecture arising from the new plastics. My feeling is that there are fair phases to the entry of foams into the housing market--and each of them is well under way in development.

- (1) Usage as an insulating material supplanting older forms. Spray, pour and slab techniques are all applicable and are being used.
- (2) Usage in building components such as foam-backed siding, foam-filled doors, curtain walls, etc.
- (3) The sandwich panel house.
- (4) The new architecture or esthetics based on free-form shapes, domes, folded-plates, and all the other geometric forms that are useful.

Note particularly that the first three phases do not require a basic change in the appearance of a house--this, I feel, is vital since the basic appearance of houses has not changed for centuries. In other words, foams can indeed be used extensively in housing without necessitating a change in esthetics.

Aiding the cause in residential use is the tremendous campaign being waged by the electric power industry to sell electric heat and air conditioning. This emphasizes the need for better insulation. It is vital, however, to be certain that foam insulation is accompanied by proper design and engineering. It is folly to put a heavy blanket of foam around a house only to have heat leaks all over the place through windows and frames, doors, studding, etc.

Participation in the non-residential building markets, which includes commercial and institutional structures, and cold

storage and process buildings, is already well under way. This is a reflection of two things--the emphasis given this market by the industry and the fact that such buildings are generally purchased by professionals as opposed to the non-professional home buyers. As such, they have been impressed by the properties of foams and buy according to a long range plan.

The balance of this market consists of pipe and tank insulation and other non-building construction. Development of foams with higher temperature resistance will open up new opportunities here--steam pipe insulation, for example.

Transportation

The usage of the cellular plastics is already well established here. One of the chief reasons for successful growth here has been and will continue to be the increased cubic capacity permitted by the more thermally efficient foams, as well as the lower dead weight usually possible.

A major breakthrough can be achieved here if the structural properties of foams are exploited. This is particularly true in automobiles, where a growing amount of research is being directed to the possibilities of foam reinforced doors, fenders, roofs, rocker panels, etc.

Increased rail usage also depends upon the redesign of railroad cars around the sandwich panel principle.

Appliances

Here, as in transportation, foam usage is well developed for obvious reasons. Further growth of this market will be dependent upon the inclusion of plastic foams in the smaller refrigerators and in such miscellaneous appliances as dehumidifiers, water coolers, dishwashers, and laundry equipment. Usage in ranges and ovens is out because of maximum service temperature limits. The development of foams with higher temperature limits (600°F for example) would signal very large increase in usage.

Packaging, Containers and Cups

Estimated to be the second largest market today for cellular plastics, this market is currently dominated by polystyrene foam--particularly in the insulated drinking cup field.

This may be the real "sleeper" among the market groupings. Forecasts have been made estimating upwards of 500 million pounds for packaging use.

Here, cost is the single, most important factor. The ideal package component costs nothing, weighs nothing, protects the contents from any conceivable damage, and presents no problems in fabrication, storage and disposal. However closely the rigid foams approach these ideals will help determine the extent of penetration into this market.

So far, pour-in-place packaging with urethane foams has been very disappointing. This is largely due to a general lack of development on the part of the molding industry and somewhat to the lack of attention given this market by the urethane producers. In time, however, we can look for the urethane foam industry to exert more R & D and marketing pressures on this usage, particularly when some of the other markets, construction, transportation and appliances, reach a more mature state.

At present, the major usage of urethane foams for packaging appear to be in container manufacture, particularly for insulated multi-function, multi-trip containers.

Other Markets

Marine usage is fairly large and relies on the flotation properties of the closed-cell foams for its existence. One of the more interesting aspects of this market is marine salvage.

Urethane foam has found a unique outlet in the mining industry, as roof and wall sealing materials and fire stoppings. It has been demonstrated that urethane foams outlast sprayed concrete on mine passageway walls and volume usage will depend on the increased acceptance of this material by the mine operators.

Military and space age markets are extremely difficult to predict. Here, economics seem to be less important and properties and methods of application are stressed. Consequently, some of the higher cost foams, such as the epoxies and phenolics, may find proportionately greater markets.

* * *

Having now reviewed the overall market potentials for the family of cellular plastics, we can now consider the individual foams and their respective penetrations into these markets.

Our view of the market place shows that only two foams are presently significant from an economic and therefore volume standpoint: the rigid urethanes and the polystyrenes.

Since our time is somewhat limited, our discussion will center on these two foams. A third foam, rigid PVC will be mentioned briefly, as it has potentially a strong competitive basis.

Rigid Urethane Foam Markets

Table IV describes rigid urethane foam markets. Note that the largest market today for urethanes is in appliances, while the forecast for the late sixties indicates a greater potential in construction and possibly, packaging. In effect, the dominance of the market by the appliance industry with a great deal to say over foam properties, economics and techniques, is declining. This is both good and bad as far as the industry is concerned; good, in that larger markets and a wider base of distribution are involved; bad, in that more intense marketing effort will be necessary to reach these diverse and widely scattered markets. The construction market, for example, is made up of literally thousands of consumers ranging from neighborhood builders and insulation contractors to the pre-fab housing industry to the building products and building component manufacturers, and so forth. This means larger sales and service staffs will be necessary to contact and solicit this business.

Markets for rigid urethane foam are growing at the rate of 45-46% per year since 1960 and continuation of this growth rate will yield the 250 million pound figure quoted. Here again, the qualifying requirements stated in Table III are the key. A spread of about 140 million pounds exists between maximum and minimum markets; in other words, this 140 million pounds is the incentive to the urethane foam industry to solve the problems stated in Table III.

Table V presents an estimate of the application methods that have been and will be involved in the forecasted markets.

Polystyrene Foam

Table VI offers a breakdown of polystyrene participation in the foam markets.

Note that the growth of construction markets closely parallels that in packaging and foam cups. These are polystyrene's two largest markets and it will be here where competition with the urethanes will be keenest.

TABLE IVRIGID URETHANE FOAM MARKETS

(millions of pounds)

<u>MARKET CATEGORY</u>	<u>1962</u>	<u>1966</u>	<u>1970</u>
CONSTRUCTION	3	30	70-160
TRANSPORTATION	4.8	32	50- 80
APPLIANCES	10	26	40- 80
MARINE	2	8	15- 50
PACKAGING	neg.	4	10-100
MISCELLANEOUS	<u>2</u>	<u>10</u>	<u>15- 30</u>
TOTAL	22	110	200-500

TABLE VRIGID URETHANE FOAMAPPLICATION METHODS

<u>METHOD</u>	<u>1962</u>	<u>1966</u>	<u>1970</u>
SLAB STOCK	10%	20%	27%
FACTORY FOAM-IN-PLACE	72%	57%	47%
FIELD POUR-IN-PLACE	9%	8%	8%
FIELD SPRAY-IN-PLACE	<u>9%</u>	<u>15%</u>	<u>18%</u>
TOTAL	100%	100%	100%

14-B

TABLE VI

POLYSTYRENE FOAM MARKETS

(million pounds)

<u>MARKET CATEGORY</u>	<u>1962</u>	<u>1966</u>	<u>1970</u>
CONSTRUCTION	26	47	85-100
TRANSPORTATION	5	4	10- 15
APPLIANCES	5	6	10- 15
MARINE	8	18	25- 30
PACKAGING, CUPS	25	59	95-110
MISCELLANEOUS	<u>9</u>	<u>31</u>	<u>25- 30</u>
TOTAL	78	163	250-300

TABLE VII

POLYSTYRENE FOAM

APPLICATION METHODS

<u>METHOD</u>	<u>1962</u>	<u>1966</u>	<u>1970</u>
EXPANDED BOARD (styrofoam)	39%	23%	20%
BEAD BOARD	17%	25%	27%
MOLDED BEAD	<u>44%</u>	<u>52%</u>	<u>53%</u>
TOTAL	100%	100%	100%

Table VII is an estimate of the types of polystyrene foam that will make up the forecasted markets.

III ECONOMICS

Now, let's see what economic factors have brought about these markets we've been talking about.

URETHANE FOAMS

Consider first, Table VIII which is an estimate of the raw material productive capacity in the urethane industry. This list is taken from the trade literature and my use of it is strictly for purposes of illustration. No endorsement of these numbers by Mobay is expressed or implied.

Perhaps the most significant fact that can be noted from this Table is the apparent surplus of capacity. For example, if we convert the foam market figures described earlier into isocyanate requirements the figures on Table IX result.

The difference between markets and capacity is substantial and suggests two things (at least).

- (1) A tremendous incentive exists for the raw materials producers to develop foam markets.
- (2) Alternate markets besides foams must be found for these raw materials.

* * *

MARKET STRUCTURE

Figure 1 offers a schematic representation of the marketing structure for rigid urethane foams.

There are four choices open to the end user insofar as source of supply is concerned. He can buy raw materials and concoct his own foams, he can use prepared foam systems or board stock or he can have the foam supplied or even applied by a distributor or applicator.

(Your notes include a fairly complete list of systems suppliers and foam board producers.)

This leads us to the problem of deciding which route to take. The answer to this problem is one of economics and volume

requirements and begins with a consideration of what does a urethane foam cost.

Table X describes, in broad terms, a typical rigid urethane foam formulation and includes raw material costs based on carload lot purchases.

You will note that there is about 30-31¢ worth of chemicals in a pound of foam. But the story has only begun. We must analyze further the value added as we move through the several distribution channels.

Table XI should help illustrate the various elements of this "value-added" factor. Note particularly the "cost of know-how" element. This is a measure of the costs of maintaining a minimum quality control, research and development effort.

It is obvious that the difference in foam costs is primarily a function of the volumes involved. Further analysis has shown that it takes about 1.6 million pounds of foam per year consumption to bring the cost of "doing-it-yourself" down to the levels quoted by the system supplier.

It is also obvious that board stock is the highest cost route of the three we've illustrated. However, it must be remembered that at this point, we've only considered the cost of the foam and have said nothing about the actual installation of the foam. In other words, all we've got is a pile of foam boards or a couple of cans of chemical system and we still have to apply the foam. We will consider the costs of installation a little later, but it can be noted here that foam board can be used without special machinery and by unskilled labor, and is therefore cheaper to use in small volumes.

In summary, a prospective foam consumer must first determine his probable volume consumption and then decide which route to follow based on the economics stated above.

POLYSTYRENE FOAMS

Polystyrene foam, whether it is of the expanded or the bead variety, depends first upon the production of styrene monomer. Table XII presents a list of styrene monomer capacities.

Of course, in contrast to the urethanes where foams are responsible for the greater part of urethane markets, it is evident from

TABLE VIIIURETHANE RAW MATERIALS CAPACITIES

(million pounds)

<u>COMPANY</u>	<u>POLYOL</u> ⁽²⁾	<u>ISOCYANATE</u> ⁽⁹⁾
ALLIED	20	50
ATLAS	25	--
DOW	60	--
DUPONT	--	70
JEFFERSON	20	--
MOBAY	--	70
KAISER	--	(20)
OLIN	25	15
UNION CARBIDE	120	30
UPJOHN	--	25 (50)
WITCO	20	--
WYANDOTTE	90	(25)
OTHERS	<u>10</u>	<u>3</u>
TOTAL	390	263 (333)

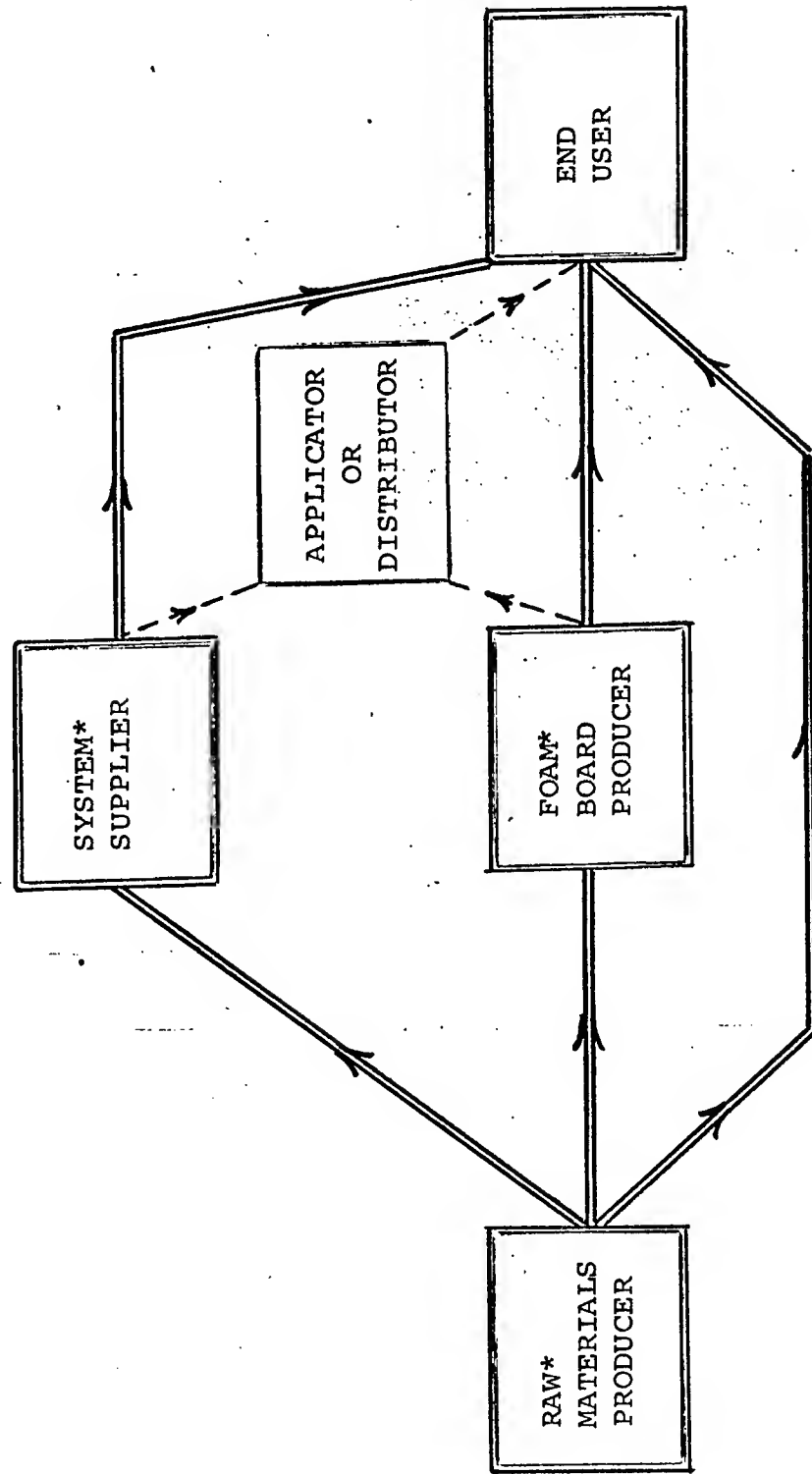
(Note: Figures in parentheses are announced capacity increases not yet on stream.)

TABLE IXURETHANE FOAMISOCYANATE MARKETS

(millions of pounds)

<u>ISOCYANATE TYPE</u>	<u>1962</u>	<u>1966</u>
TDI	55	115
POLYMERIC AND CRUDE	5	35

FIGURE 1

URETHANE FOAM MARKETING STRUCTURE

* SEE APPROPRIATE LISTS IN TEXT

TABLE X

RAW MATERIAL COSTS
OF
RIGID URETHANE FOAMS

<u>RECIPE</u>	<u>LARGE PURCHASER</u> (5 million pounds ⁺)	<u>SMALL PURCHASER</u> (½ million pounds)
POLYOL	100 pbw @ 24¢/lb = \$24.00	@ 29¢/lb = \$29.00
BLOWING AGENT	35 pbw @ 19¢/lb = 6.65	@ 23¢/lb = 8.05
ADDITIVES	3 pbw @ 200¢/lb = 6.00	@ 200¢/lb = 6.00
ISOCYANATE	<u>105 pbw @ 34¢/lb = 35.70</u>	@ 39¢/lb = <u>40.90</u>
	243 parts \$72.35	\$83.95
	+2% loss <u>1.45</u>	+2% loss <u>4.20</u>
	\$73.80	\$88.15

$$\frac{\$73.80}{243} = 30.4\text{¢/lb}$$

(5.07¢/bd ft)

$$\frac{\$88.15}{243} = 36.3\text{¢/lb}$$

(6.05¢/bd ft)

TABLE XI

VALUE ADDED TO RAW MATERIAL COSTS

	<u>SYSTEM SUPPLIER</u>	<u>DO-IT-YOURSELF</u>	<u>BOARD STOCK</u>
VOLUME	5 million pounds	$\frac{1}{2}$ million pounds	5 million pounds
RAW MATERIAL COSTS	30.4¢/lb	36.3¢/lb	30.4¢/lb
COST OF KNOW-HOW	1.3	13.2	1.3
EQUIPMENT AMORTIZATION	1.2	6.0	6.0
OPERATING COSTS	2.6	6.4	24.7
12% PRETAX PROFIT	<u>4.8</u>	<u>0.0</u>	<u>8.5</u>
TOTAL	40.3¢/lb	61.9¢/lb	70.9¢/lb
	(6.72¢/bd ft)	(10.32¢/bd ft)	(11.81¢/bd ft)

16-D

consideration of Table XII that styrene foams are only a very small part of the total styrene market. This is further evidenced by Table XIII which lists the capacities of the various expandable bead producers.

All of these producers use a process based on the batch process developed by Badische, Anilin and Soda Fabrik (BASF) which was described earlier this week.

The list does not include an estimate of capacity for expanded board (Styrofoam - Dow Chemical Company).

In addition to these companies who are basic in bead manufacture, styrene foam is available in bead-board form from a great number of producers who use purchased beads as raw materials. There are also a great number of molders who produce molded foam objects such as cups and packaging components from purchased beads.

* * *

The economics of polystyrene bead foam manufacture is presented in Table XIV.

A summary of the economics of polystyrene expanded foam is presented in Table XV.

COMPARATIVE PROPERTIES

We have now carried our discussion to the point where we can begin to evaluate the differences between the two major foams as regards properties and installation costs.

Table XVI provides information regarding the relative efficiencies of the foams and other materials used as thermal insulation.

If structural strength is also important (and recalling our discussion on markets, it must be), then the data in Table XVII is meaningful.

The decision to use one foam instead of the other will be based in part on the data in Tables XVI and XVII but only after careful consideration of all the requirements of the specific end use--especially such factors as insulation requirements, maximum service temperatures, dimensions, structural load bearing, production volume, other materials to be included in the composite structure, and of course, fabrication and installation techniques desired.

INSTALLATION COST FACTORS

It is almost impossible to make any general estimates on the cost of installing or fabricating with foam without considering the individual application. Just as the unique requirements of the end use will in part dictate the selection of the foam to be used, likewise these requirements will determine the application technique and its costs.

Perhaps I can best be of service by making whatever general statements I can and then describe some specific examples which are fairly well documented which should illustrate typical applications.

To begin with, the problem is not nearly so complex when considering the use of board stock, either styrene or urethane. Here, three things primarily enter into the installation cost picture: labor cost, adhesive cost and scrap.

Machinery requirements for slab lamination are fairly simple. The adhesive must be applied by spray or by brushing and the foam laminated by presses or rollers or by hand.

Surface preparation is, of course important, but aside from the adhesive and its application, it is usually only necessary to have a clean and dry substrate to work with.

Some selectivity is necessary as regards adhesive selection. While the urethanes can use solvent-based adhesives, which may or may not require heat for activation and cure, care must be exercised when using slab styrene foam because of its lower solvent resistance and temperature resistance.

Working with board stock is no more difficult than working with conventional building materials, so unskilled or semi-skilled labor can be employed.

Scrap can be a problem, particularly if oddly shaped parts are being produced.

In general, I have seen published estimates that place the cost of slab lamination at anything from 2-5¢/glue line, or in the case of a sandwich panel, 8-20¢/sq. ft. plus material cost including allowance for scrap generation.

TABLE XIISTYRENE MONOMER CAPACITIES

(million pounds)

<u>COMPANY</u>	<u>CAPACITY</u>
DOW	800
MONSANTO	600
UNION CARBIDE	410
SHELL	210
AMOCO	200 (announced new plant)
SINCLAIR-KOPPERS	270
FOSTER GRANT	150
CODEN	90*
ODESSA STYRENE	80
MARBON	75
SUNRAY - Mid-Continent	<u>60*</u>
	2945

* via direct ethylbenzene recovery--others synthesize from ethylene and benzene

TABLE XIIISTYRENE BEAD CAPACITY

(million pounds)

<u>COMPANY</u>	<u>CAPACITY</u>
KOPPERS	75
DOW	30
MONSANTO	20
UNITED CORK	15
FOSTER GRANT	<u>5</u>
	145

TABLE XIVECONOMICS OF POLYSTYRENE BEAD FOAM PRODUCTION⁽¹⁾

<u>BEAD SOURCE</u>	<u>PURCHASED AT 37¢/lb.</u>	<u>MANUFACTURED AT 22¢/lb.</u>
Volume	515,000 lbs.	515,000 lbs.
Board Foot Sales (1.2 pcf)	6.15 mm lbs.	6.15 mm lbs.
Total Cost of Product Sold	4.83¢/bd. ft.	3.55¢/bd. ft.
Sale Price	7.8¢/bd. ft.	7.8¢/bd. ft.

TABLE XVECONOMICS OF EXPANDED POLYSTYRENE FOAM⁽¹⁾

	<u>POLYSTYRENE CHARGED AT COST</u>	<u>POLYSTYRENE CHARGED AT MARKET PRICE</u>
Volume	5.2 mm lbs.	5.2 mm lbs.
Board Foot Sales (1.8 pcf)	35 mm bd. ft.	35 mm bd. ft.
Estimated Total Cost of Product Sold	4.5¢/bd. ft.	5.4¢/bd. ft.
Selling Price (avg.)	8.5¢/bd. ft.	8.5¢/bd. ft.

TABLE XVI

COMPARATIVE EFFICIENCY OF
COMMERCIAL INSULANTS

<u>MATERIAL</u>	<u>PRICE</u> (¢/bd. ft.)	<u>K-FACTOR</u> (BTU-in/hr-ft. ² -°F)	<u>EFFICIENCY FACTOR</u> (price x k-factor) ⁻¹ \$
Poured Polyurethane	7.5-10	0.11	91-125
Fibrous Glass	4.5-7	0.24	59-91
Expandable Polystyrene	7-8.5	0.24	50-59
Slab Polyurethane	14-18	0.15	37-48
Expanded Polystyrene	8.5-10	0.25	40-48
Rigid PVC Foam	17-20	0.17	29-35
Foamed Glass	11-13	0.40	19-23

18-C

Example, for PU, price = 10¢/bd ft = \$/10

$$\frac{1}{10 \times 11} = \frac{1}{110} = 90.9$$

Aptf

TABLE XVII

COMPARATIVE PHYSICAL PROPERTIES

OF

RIGID CELLULAR PLASTICS

MATERIAL	DENSITY (pcf)	COMPRESSIVE		SHEAR		K FACTOR (BTU-in/hr-ft ² -°F)	FIRE* RESISTANCE (ASTM 1692)
		STRENGTH (psi)	STRENGTH (psi)	STRENGTH (psi)	MODULUS (psi)		
Polyurethane	1.5-2.0	20-60	20-50	20-50	250-550	0.11	SE or non-burning
Polyurethane	2.1-3.0	35-95	30-70	30-70	350-800	0.11	SE or non-burning
Polyurethane	3.1-4.5	50-185	45-125	45-125	500-1300	0.12	SE or non-burning
Expanded Polystyrene	1.7-2.3	16-38	30-40	30-40	1000-1300	0.25	SE (melts at 175°F)
Expandable Polystyrene (Bead)	1.2-1.5	10-13	20-30	20-30	500-600	0.24	SE (melts at 175°F)
Rigid PVC Foam	1.6	30	30	---	---	0.17	SE or non-burning

18-D

* if suitably formulated

Molding with expandable styrene beads is a fairly well established technique, representing about half of the total market for styrene foam. Depending upon the size of the molded part and the volume produced, conversion costs may run anywhere from twice the value of the beads to ten times their value. On the average, a conversion factor of 3 to 6 times bead cost would be a good general figure.

An excellent discussion of the economics of expandable bead molding is available in the literature⁽⁷⁾. Table XVIII from that reference itemizes the costs of molding a small 34-gram part.

* * *

As far as costs of foamed-in-place urethane are concerned, here again, the size of the object and its production volume will have a large bearing on foaming costs.

Since some type of foam machine will be required, this aspect should be the first to be considered. Foam machines can be as simple as a hand drill powered paint mixer type for small volume pours; portable spray equipment delivering two to ten pounds of spray foam per minute and costing less than \$5,000; stationary foam machines for larger volume pours, delivering anywhere from 10 pounds per minute to 200 pounds per minute and representing capital investments of from \$10,000 to over \$100,000.

Molds, jigs and fixtures will also vary in cost with the particular part to be foamed. Jigging is quite important as the pressures generated by the rising foam can range from almost nothing to as much as 70 psi in special cases.

Labor costs will tend to run higher since skill and techniques are very important in foaming in place.

Perhaps the best way to illustrate foaming-in-place costs would be to describe a number of typical examples for which such data has been published.

One such case is described in Figure 2 which shows the relative costs for materials, labor and miscellaneous items in the insulation of a storage tank.

Another fairly well documented case is that relating to the production of station wagon floors in a prototype study conducted by a major steel company and an auto body fabricator.

They showed that a sandwich panel floor could be constructed using urethane foam as a structural core and which would produce a floor that was 15% stronger, 40% stiffer, and 25% lighter and at a costs savings of approximately \$2.00 per floor or 5% less. Capital requirements for a 300 floor per day volume were approximately \$70,000 of which \$23,000 was required for foaming equipment. Foam installation costs were approximately 6.5¢/sq. ft. of foam installed (3/4" thick).

A complete discussion of the equipment system typical to that used in the manufacture of household appliances by pour-in-place techniques appears in the literature⁽⁶⁾.

Recent developments in both equipment and chemicals have focused considerable attention on the spray-in-place application of rigid urethane foam. One such development involves the use of sprayed foam and ordinary chicken wire in the insulation of a large apartment structure. A 3/4 inch coat of foam was sprayed at a cost of 14-15¢ per sq. ft. (including the supplemental reinforcing chicken wire) replacing standard wall insulation, furring and rock lath normally costing 23¢ per sq. ft. The resulting foam layer served as both insulator and a base for plaster.

Another spray application, involving 50,000 sq. ft. of coverage with 3/4" of foam and two coats of paint was claimed to involve 10¢/sq. ft. material cost. Application time was 104 man-hours, divided 56 man-hours for the foam application and 48 hours for the top coat. At normal wage rates for semi-skilled labor this works out to about 12¢/sq. ft. installed.

The spray insulation of conventional residential construction involving stud-walls is becoming more attractive. At present costs, it appears that a contractor could compete with batt insulation if he could spray two normal sized homes per day per machine per two man crew. Projects now underway show promise of meeting this tight schedule.

It is, of course, sheer folly to compare installed costs of urethane foam with installed costs of fibrous glass for example, strictly on the basis of comparative insulating value. This completely omits consideration of the structural value of the

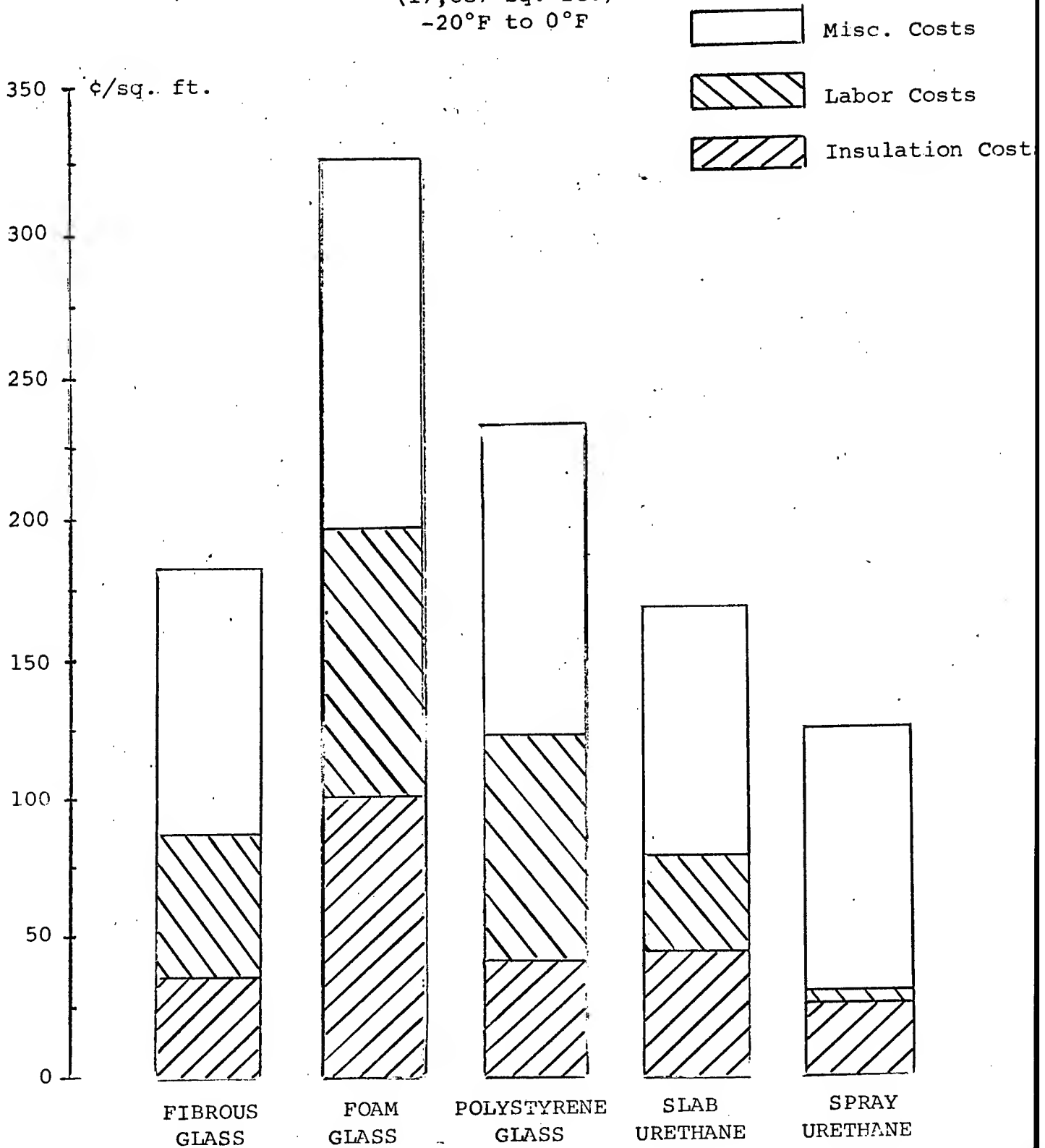
TABLE XVIIIEXPANDABLE BEADMOLDING COST ESTIMATE

Material weight, gms.	34	
7% Adjustment for scrap plus gas loss, gms	36	
Estimated machine cycle time, sec.	90	
Estimated cycles per hour	40	
Cycles per hour adjusted to 90%	36	
No. of cavities - 10, packs	5	
Packages per hour	180	
Material cost (31¢/lb.) \$		4.50
Labor		
Operator $2.50 \div 4$, \$.60	
Material handler at $1.60 \div 4$, \$.40	
Supervision at $4.00 \div 8$, \$.50	
Maintenance at $2.40 \div$.30	
Labor cost, \$		1.80
Overhead		
Labor X 125%, \$	2.25	
600 lbs. steam (.16 per 100 lb.), \$.96	
Electricity, \$.27	
1000 gal. water (at .012 per 100 gal.), \$.12	
Mold amortization ($\frac{2400}{600}$), \$	4.00	
Depreciation on equipment, \$	2.30	
Overhead cost		<u>9.90</u>
Total cost per hour, \$		16.20
Manufacturing cost per unit, \$.09
Packaging, freight, sales and profits (50%), \$		<u>.045</u>
Total cost, \$.135

FIGURE 2

RELATIVE COSTS OF VARIOUS INSULATION
MATERIALS ON A STORAGE TANK⁽¹⁾

(17,687 sq. ft.)
-20°F to 0°F



foam (fibrous glass, for example, has no structural value). Perhaps the best illustration of that is the classic case of the architectural curtain wall. A major producer of curtain walls formerly used 18 gage (0.0478") steel skins and fibrous glass insulation, but found that by using poured-in-place urethane foam, the skin thickness could be cut in half, to 24 gage (0.0239"). This is due to the structural contribution of the foam core, acting as a structural laminate. The reduction of steel thickness represents a savings of 2 pounds of steel per square foot of panel and at current prices of steel, amounts savings of from 16¢ to as much as \$1.00 per square foot. This savings is attributed to the use of foam and in some cases, will pay for the foam.

Before a true comparative cost study can be completed, it is therefore necessary to take into account, the probable savings in materials and fabrication of associated materials of construction, such as the metal skins in a sandwich panel.

SUMMARY OF ECONOMICS

I appreciate that the foregoing discussion of economic factors was somewhat vague and surely leaves several questions unanswered in your minds. But that is the nature of the subject.

If there is any general statement that can be made regarding cellular plastics economics, it is probably this:

No economic evaluation of foam usage is possible without consideration of all the aspects of the proposed operation. Foams are more than just good thermal insulators--they offer structural values, savings in related materials of construction, novel methods of fastening and coating, savings in fabricating procedures and costs, to name a few--consequently all of these aspects of manufacture must be evaluated.

The rapid rate of growth of foam markets is testimony to the benefits offered by these materials and is evidence that when all of these aspects of manufacture are considered, the usage of rigid foams increasingly satisfies the needs of the job.

BIBLIOGRAPHY

1. Einhorn, I. N., "Economics of Cellular Plastics," lecture at University of Michigan Engineering Summer Conference, Cellular Plastics, August 3-7, 1964:
2. Tenhoor, R. E., "The World Market for Urethane Chemicals," Chemical and Engineering News, 41, No. 5, p. 94-104, February 4, 1963.
3. Noren, H. H., "Western Hemisphere Markets for Cellular Plastics," Journal of Cellular Plastics, 1, No. 1, p. 242-249, January 1964.
4. Shedd, D. P., "Accomplishments of Today - Promise of Tomorrow of Cellular Plastics," S.P.I. 7th Annual Technical Conference Proceedings, p. 2-Q, April 1963.
5. Brookes, C. E., "Elastomer Latices," Proceedings of Chicago Meeting, Elastomers 1963-1968, The Chemical Market Research Association, CMRA paper 440, February 1964.
6. Wolfert, C. K., "Systems for Foaming Urethane Refrigerator Insulation," Modern Plastics, March 1965, p. 129.
7. Thomas, R. H., "Economics of Conversion of Foam Beads to Useful Packaging Shapes," a paper presented at S.P.E. RETEC, "Thermoplastic Foams for Rigid Packaging," November 4, 1965.
8. International Foamed Plastics Markets and Directory, Technomic Publishing Company, published annually.
9. Oil, Paint and Drug Reporter, March 28, 1966, p. 49.

URETHANE FOAM SYSTEMS MANUFACTURERS

Applied Plastics Division, El Segundo, California
Archer Daniels Midland Co., Los Angeles 22, California
Callery Chemical Company, Callery, Pennsylvania
Chase Chemical Corporation, Pittsburgh 1, Pennsylvania
Conap, Inc., Allegany, New York 14706
Cook Paint & Varnish Co., North Kansas City, Missouri
Flexible Products Corp., Marietta, Georgia
Freeman Chemical Corp., Port Washington, Wisconsin
General Latex & Chemical Corp., Cambridge, Massachusetts
General Plastics Company, Tacoma, Washington
The Glidden Company, Cleveland 2, Ohio
Reading, Pennsylvania
San Francisco, California
Hooker Chemical Corporation, Niagara Falls, New York
Isocyanate Products, Inc., New Castle, Delaware
Nopco Chemical Company, Newark, New Jersey
Pelron Corporation, Lyons, Illinois
Phelan's Resins & Plastics, Burlington, Iowa
Pittsburgh Plate Glass Co., Pittsburgh, Pennsylvania
Polytron Company, Richmond 4, California
Reichhold Chemicals, Inc., Azusa, California
White Plains, New York
Ferndale, Michigan 48220
Rinshed-Mason Company, Detroit 10, Michigan
Anaheim, California
Windsor, Ontario, Canada
Unarco Industries, Inc., Bloomington, Illinois

RIGID URETHANE FOAM MANUFACTURERS

Atlas Chemical Company, Inc.
Wilmington 99, Delaware

Dacar Chemical Products Co.
Pittsburgh 20, Pennsylvania

Dow Chemical Company
Midland, Michigan

General Plastics Company
Tacoma, Washington

Hardigg Industries
S. Deerfield, Massachusetts

Johns-Manville Sales Corp.
New York 16, New York

Monsanto Canada Limited
Oakville, Ontario, Canada

National Gypsum Company
Buffalo 2, New York

Pelron Corporation
Lyons, Illinois

Pittsburgh Corning Corp.
Pittsburgh, Pennsylvania

Unarco Industries, Inc.
Bloomington, Illinois

U. S. Mineral Wool Co.
Stanhope, New Jersey

10214-16

CHEMICALLY CROSSLINKED POLYETHYLENE FOAM

May, 1967

Yoshio Kadowaki

Central Research Laboratory

The Furukawa Electric Company, Ltd.

Futabacho Shinagawaku, Tokyo, Japan.

To be presented at the 1967 Polymer Conference Series

Wayne State University

Chemically Crosslinked Polyethylene Foam

Introduction

The foamed plastics which are now being commercially used in Japan are foamed polyurethane, foamed polystyrene, foamed PVC, foamed phenol, foamed polyurea, and so forth. Among them, foamed polyurethane and foamed polystyrene are produced in quantities.

In Japan recently the manufacturing technique for highly expanded PE foam has been developed and about ten companies have started the manufacture of cellular PE. It is only in the past couple of years that highly expanded PE foam was first produced in Japan. Now that its good properties are known, the market for this material is being much developed, and a further rapid development is to be expected in the future. Japan's cellular plastics industry now begins watching it closely as "a third foam" after polyurethane foam and polystyrene foam.

What is interesting about this is the fact that several different processes of PE foam have been developed almost at the same time and products are sold by various companies. In this paper I am going to touch chiefly on the manufacturing process, features and use of the foamed PE we are now developing by chemically crosslinking method and lastly mention the trend of Japan's PE foam industry.

1. Preparation of PE foam

A. History of PE foam in Japan

It was for wire coating material for communication cable that foamed PE was used for the first time. Since around 1958 it has practically been used, foaming aimed at improvement of dielectric power factor of PE for covering. The foaming process was the one for foaming simultaneously with extrusion by the use of blowing agents. Recently, a new process has been developed which expands PE by quickly heating a wire coated with high-density PE solution. And this is replacing the old process. This process has been established by the Furukawa Electric Co. The product obtained is a high-density foamed PE with a density of around 40-50 pcf, which has excellent electrical properties and mechanical strength. In other fields than electric wires and cables, a fairly high-density (29-37 pcf) foamed PE sheet has been produced since 1962 in Japan. Another company has developed sheets and inflation films and blow-molded material of high-density foamed PE (28 pcf) since 1965. These products are made by extruding process using solvent type blowing agent.¹⁾ Conditions of extruder operation must be severer than ordinary conditions. These high-density PE foams (28-37 pcf) have a relatively high strength and are used for core material or soft structural materials. But at present high-density foamed PE is mostly used for coating of communication cable. It was only in recent years that highly expanded PE foam having a density of 2-7 pcf was developed. The delay in the development of highly expanded PE was due to the difficulty in manufacturing technique.

In Japan, at present it is produced roughly by the following methods.

- a) Extruding method
- b) Ionizing radiation method
- c) Chemically crosslinking method
- a) Extruding method

This is a method developed by Dow Chemical Co. (U.S.A.).²⁾

The products are slabs, rods, and so forth having relatively large cells (about 50 mil).

- b) Ionizing radiation method

This is a method in which PE containing blowing agent is cured by ionizing radiation and heated so as to decompose the agent and thus foam is manufactured. By crosslinking, the viscoelasticity of PE at high temperature is increased and individual cell is kept in a stable condition without rupture or agglomeration until it is cooled, and thus low-density foam is obtained. The product is a long sheet of a thickness of 1/4" or under and its cells are closed ones of comparatively small size (about 10 mil).

- c) Chemically crosslinking method

In this process, crosslinking is carried out by the use of chemical crosslinking agents. It will be described in detail in the next item. The products are slabs of very small cells (2-3 mil) and long sheets of medium cells (about 20 mil). The details of the techniques in question belong to the know-how of the makers concerned and are hardly made known. Their manufacturing techniques are in course of development and it is likely that much better processes will be developed in the future, together with cut in cost.

B. Manufacturing chemically crosslinked polyethylene foam

1) General Principles

It is generally to be considered that there is an optimum viscoelasticity range in plastic foam manufacture. If it is too high, plastics do not expand, while if too low cells are so weak as to rupture or agglomerate, and thus no low-density PE foam is obtainable. From the manufacturing conditions for polystyrene foam, I presume that the elastic modulus suitable for expanding molten plastics is $10^5 - 10^7$ dyne/cm² order. Theoretically, there ought to exist a temperature range having such viscoelasticity, but actually this temperature range is very narrow, and no satisfactory foaming is possible simply by foaming temperature control, on the case of PE. PE is converted into gel by curing with crosslinking agent and has a fairly high viscoelasticity even above the melting point. As this cross-linked PE keeps a fairly constant viscoelasticity in wide temperature range, there is a wide latitude of foaming temperature. We can also keep the viscoelasticity of material at any given level at any temperature by changing crosslinking rate, and thus obtain highly expanded PE foam.

2) Curing agent.

The typical curing agents for PE are organic peroxides such as dicumyl peroxide, 2,5-dimethyl-2,5-di (tert. butyl peroxy) hexane, 2,5-dimethyl-2,5-di (tert. butyl peroxy) hexyne. Their decomposition temperatures are respectively ca. 295° F, 310° F, and 320° F. They are used according to the kind of PE and foaming process. Characterization of crosslinked PE

in foaming conditions is not simple. This is because we must consider both viscosity and elasticity as well as surface tension of crosslinked PE; since material heating is done not statically but dynamically in PE foaming process, we have to take into account the correlation between crosslinking rate and foaming agent decomposition rate.

It is usually the case to express the characterization of cross-linked PE suitable for foaming in terms of gel content. Gel content is a measure of characterization of crosslinked PE fit for foaming. Increase of gel content represents the increase of viscoelasticity of crosslinked PE. While it has been pointed out that gel content of crosslinked PE suitable for foaming is 10-60%³⁾, the result of our studies shows that 30-85% is suitable. If gel content is small, there is apt to be an increase in cases of cell rupture and agglomeration. Therefore, cell diameter becomes large and no highly expanded cellular material is obtainable. According to increase in gel content, cells decrease in size and good low density foam is obtainable. But if gel content increases beyond that, swelling is obstructed, and low density foam cannot be obtained. In some cases, cracks occur partially.

Even in case of foamed PE having the same density, the more crosslinking agent is used, the higher compression modulus the product has. This is because, I think, cell sizes become fine and uniform, their film thickness also becomes uniform and further, crosslinked cell film is highly oriented through expansion.

3) Foaming agent

Heat-decomposing type blowing agent is used for the manufacture of chemically-crosslinked PE foam. Typical ones for polyethylene foaming are (i) azobisformamide (decomposition temperature; ca. 392° F) (ii) dinitrosopentatetramine (decomposition ca. 327° F) and (iii) 4,4'-oxybis-(benzene sulfonylhydrazide) (decomposition ca. 400° F).

A special care must be taken of the following points in selecting a foaming agent.

i) Decomposition temperature.

Especially, this must be considered in relation to the decomposition temperature of crosslinking agent and the foamed polyethylene manufacturing method. To produce foamed polyethylene with fine closed cells, a blowing agent having a higher decomposition temperature than cross-linking agent must be selected. It is advisable to use a blowing agent having a decomposition temperature close to that of cross-linking agent to obtain PE foam with open or coarse cells.

ii) Powder size and dispersitivity.

Needless to say, a blowing agent of a small grain size is desirable; but it must not develop coagulation when dispersed in polyethylene.

iii) Kind and volume of evolving gas.

The blowing agent must evolve as much gas as possible; but such gas must preferably be as odorless and harmless

as nitrogen gas. A blowing agent that generates CO_2 gas is not suitable because it causes the density of foam to change with time in some cases, owing to diffusion of the gas.

iv) The blowing agent must not adversely affect the cross-linking agent or other additives.

v) Cost.

From the technical viewpoint, azobisformamide is the best blowing agent for polyethylene, and its decomposition temperature can be controlled by additives. Its only demerit is high cost.

4) Foaming process

Fig. 1 is the process diagram of cross-linked polyethylene foam manufacturing process.

First, cross-linking agent, blowing agent, and, when required, pigment and filler are added to polyethylene and thoroughly mixed by Banbury mixer, mixing roll, extruder, or powder mixer. This mixing must be done at such low temperature as will not cause decomposition of cross-linking agent and blowing agent. To produce cells of uniform diameter in the polyethylene foam, it is necessary to mix the materials as uniformly as possible.

Then, shaping is done by extruder equipped with T-die, calender, or mold to shape the compound into sheet or slab. Temperature must be controlled also in this process to prevent decomposition of cross-linking agent and blowing agent, because such decomposition will cause some structural defect in the foam and make its cell diameter uneven.

The raw material for shaping is usually in pellet or powder form. Various means are being worked out by many companies concerned to produce shaped foam product free from voids or any other defect. The most important step in the process is heating and foaming. The cell structure of finished product greatly varies according to how the crosslinking agent and blowing agent are decomposed. Although we have aimed at controlling the size and structure of cell and expansion rate at will, we have not yet fully clarified its mechanism. Generally, fine closed type cells develop when the foaming agent is decomposed after complete cross-linking, while open or coarse cells are produced when cross-linking is made after decomposition of the blowing agent. If the blowing agent decomposes before crosslinking is completed, there develop slightly larger closed cells in the foam. Throughout these processes, the most important is the selection of blowing agent and cross-linking agent as well as heating device and heating condition. Dr. Lasman's report⁴⁾ covers a method of decomposing the cross-linking agent and blowing agent in a mold under high pressure and ejecting the foam product from the mold. In the conference of last year, Dr. Benning made a detailed report about it. The same method seems to be practised by a few Japanese companies.

5) Types of foamed polyethylene products.

Low-density chemically cross-linked foamed polyethylene is commercially available in three foams, that is, (a) slab, 3.3 ft-wide, 6.6 ft-long, and 2 in-thick, (b) long-length sheet, 3.3 ft-wide, and 0.2 to 0.6 in-thick, and (c) shaped material.

- (a) Slab has very fine closed cells, 3 mil or under in average diameter, and a density of 1.0 to 6.2 pcf. This is batch system.
- (b) The sheet has a cell diameter of about 10 mil and a density of 1.9 to 12.5 pcf. This is made by continuous process.
- (c) The shaped material is now chiefly made for buoy for fishing and has a density of about 5-20 pcf. This is made by batch process. The cell diameter is 30-50 mil on the average, larger than those of the slab and sheet.

2. Characteristics of chemically crosslinked PE foam

Generally, the plastic foam has the properties of plastic material and those resulting from its structural factors such as expansion rate and cell structure. The chemically crosslinked polyethylene foam has three features. They are a) features peculiar to polyethylene, b) features that come from crosslinking, and c) features resulting from chemical crosslinking,

The features peculiar to polyethylene are

- (1) It makes flexible, strong, and semi-rigid cellular material,
- (2) Outstanding shock absorbing characteristic,
- (3) Low water absorption,
- (4) Superior chemical resistance,
- (5) Excellent electrical properties,
- (6) Bright colouring possible,
- (7) Harmless to humans and does not corrode any surrounding metal, etc., and
- (8) Good processability.

On the other hand, it has a defect of being inflammable.

The features produced by crosslinking are

- 1) Very fine uniform closed cells, therefore,
- 2) Looking fine and smooth to touch,
- 3) Outstanding heat insulation,
- 4) Most excellent in weather proofness of all cellular materials and
- 5) Can be manufactured with a density as low as 1 pcf, very soft to touch.

The features resulting from chemical crosslinking are

- 1) Can be manufactured in a large size, that is, thicker than 2 inches, while the maximum thickness of foamed polyethylene made by ionizing radiation method is 1/4 inch, and
- 2) Any optional size and structure of cell can be obtained according to the kind and combination of crosslinking agents and the manufacturing method employed, which in turn makes it possible to obtain any optional characteristics of the foam product.

Of course, a method is in practice for improving the properties by adding EVA copolymer or rubber besides using high-density PE for raw material PE.

Next I am going to explain by illustration the main characteristics of chemically crosslinked PE foam.

A. Tensile property

Fig. 2 and 3 show the relationship between the tensile strength, breaking elongation, and density of foam. As shown in them, sheet and slab have different properties, the strength of the latter being

higher with smaller elongation. This is due to different cell structures and cell strengths resulting from difference in manufacturing process. Slab, which has small cell diameter, uniform cell film thickness, and high cell strength has a higher strength. For reference, polystyrene foam and polyurethane foam are given in the same figure.

B. Compression characteristics

The relationship between the compression strength of chemically crosslinked PE foam under compression load at 25% deflection and foam density is shown in Fig, 4. In this case also, slab and sheet have different compression strengths, the former having a higher value. This is also to be considered due to differing cell structures and cell strengths . Comparison with polystyrene foam and polyurethane foam given for the sake of reference shows that PE foam is semirigid foam that stands midway between polystyrene foam and polyurethane foam.

Fig, 5 shows compression-deflection curves of a few samples. The area encircled by hysteresis loop corresponds to energy absorption. It is to be known that crosslinked PE foam has a large area and a good absorption of applied energy.

The problem in PE foam is that its deflection does not return to normal even when compression force is removed. Fig, 6 shows its compression permanent set. Slab has a smaller compression permanent set and is fit for cushioning material. The smallness of compression permanent set is considered due to high closed cell rate. This residual deflection is gradually recovered, and when left as it is for a week, goes back almost to the original condition.

Fig,7 shows compression set in case of repeated compression test at 50% deflection. Even after 100,000 repeated severe compressions, the deflection is only 15% or so. Fig 7 also shows compression load at 25% deflection after the same repeated compressions. Change in compression strength due to repeated compressions is relatively small, which shows that crosslinked PE foam, especially slab, is fit for cushioning material.

C. Dynamic loading property

Fig,8 shows the dynamic loading curves of a number of foams made by different methods. Crosslinked PE foam shows a low G value (peak deceleration) in a wide static stress latitude, which indicates that it is an excellent cushioning material. Crosslinked PE foam of density 2 - 3 pcf has a very good loading property in a static stress latitude of 0.3 - 1.5 lb/in².

D. Water absorption

Fig. 9 shows a comparison of crosslinked PE foam slab and polystyrene foam immersed in water under normal pressure, while Fig 10 shows water absorption rates of crosslinked PE foam buoy (density ca. 14 pcf) and rubber sponge buoy obtainable on the market subjected to water absorption test under high pressure. It is to be known that crosslinked PE foam has a very low water absorption rate.

E. Water vapor permeability

Fig,11 shows the water vapor permeability of crosslinked PE foam, polystyrene foam and rigid polyurethane foam. It shows that PE foam has by far the best property.

F. Heat insulation

Fig. 12 shows the heat conductivity of crosslinked PE foam,

Roughly speaking, it has almost the same conductivity as polystyrene foam and polyurethane foam, and a less heat conductivity than non-crosslinked PE foam, indicating an excellent heat insulation.

This is due to the fact that its cell diameter is very small and that no gas convection occurs in cells.

G. Weatherproofness

The most noteworthy feature of crosslinked PE foam is that it has the best weatherproofness of all plastic foams. Fig. 13 shows the results of outdoor exposure test of crosslinked PE foam together with polystyrene foam, polyurethane foam and PVC foam. Crosslinked PE foam which was exposed to the weather for one year remains almost unchanged in appearance and size, while the other foams developed a remarkable change in size and deterioration. Though not shown in this photo, non-crosslinked PE foam was inferior in weatherproofness. The reason for this difference is not clear. Table 1 shows the result of accelerated degradation of various kinds of foams by the use of weatherometer. In all respects, such as size, shape, strength, color change, etc., crosslinked PE foam is the best of all.

H. Service temperature

The maximum service temperature of crosslinked PE foam is 176 °F. Beyond that, it gradually develops shrinkage. If for a short while, it can be used up to 212 °F. On the other hand, it is usable down to - 184 °F, at which the foam becomes brittle.

I. Resistance to chemicals

Chemically crosslinked PE foam is excellent in this property. It slightly swells when immersed for a long time in carbon tetrachloride, aromatic hydrocarbon, gasoline, or the like, but it remains un-

affected by long immersion in acids or alkalis, there being no change in strength.

J. Other properties

The electrical properties are equal to or even better than those of material PE. Its specific volume resistivity is 10^{17} ohm-cm and its dielectric constant at 10^6 cycles/second is 1.05-1.07, the dielectric loss being 0.01%. Crosslinked PE foam, while flammable, emits no poisonous gas when it burns. Its burning speed measured according to ASTM-D-1692-59T is 1.0-2.5 in./second.

Crosslinked PE foam is not fit material for sound absorber because it consists of closed cells.

3. Working of chemically crosslinked PE

As PE foam is no specific foam, though it is a new material, most of working methods hitherto used for polyurethane foam and polystyrene foam, that is to say, cutting, punching, slicing, etc., can be applied as they are. The working method peculiar to PE foam is as follows.

A. Heat sealing and laminating

Crosslinked PE foam sheet can easily be sealed with ordinary heat sealer for films. Ordinary laminating technique makes it possible to laminate it with plastic films and its coating can be done by heat bonding to metal foil, cloth, etc.

B. Compression molding, vacuum forming and embossing

Compression molding and vacuum forming can easily be carried out for crosslinked PE foam, and various shapes can be produced. These thermoforming methods are important for crosslinked PE foam.

Compression molding is done in such a way that PE foam is heated in mold at 250 °F to 300 °F and molded by compression for

a few minutes and that the mold is cooled with water for taking the product away. For vacuum molding, ordinary type of vacuum molding machine for plastics can be used as it is. It is desirable that the machine should be equipped with heating device on both surfaces.

Vacuum molded sheets of thickness, 1/10 in. to 1/2 in. can be produced if conditions are suitably selected. It is necessary to select somewhat delicate conditions for deep-drawn products or thick sheets.

Crosslinked PE foam is stable at considerably high temperature and its cells are hardly liable to rupture, so that there is a wide latitude in working conditions, and its working is to be done easily. Moreover, crosslinked PE foam sheet can easily be embossed.

D. Adhesion and printing

PE is very difficult of adhesion or printing. On the other hand, adhesion and printing of crosslinked PE foam are good. Especially, easy adhesion and printing can be done of the sliced surface. Suitable adhesive is rubber-base. Emulsion type adhesive is not desirable. Neoprene base adhesive is the best.

4. Applications of crosslinked PE foam

By reason of its excellent cushioning, softness, heat insulation, water resistance, weatherproofness, fine appearance, and so forth, cross-linked PE foam is now used for a number of purposes. The belowmentioned are the chief uses.

A. Packaging material

Because of its flexibility and good cushioning characteristics, PE foam is widely used as packaging material. Chemically crosslinked PE foam has tiny cells and fine appearance, and its vacuum molded or compression molded products are used for packaging material, ornamental

and otherwise, for precision appliances and highgrade products.

B. Cushioning material

For its good cushioning property and little compression set, crosslinked PE foam is used as cushioning material, for example, core material for sofa, chair covering, undercarpet, sport protector, etc.

C. Heat insulating material

Crosslinked PE foam, because of its good heat insulating property, is used to keep things warm or cold. Usually, low-temperature heat insulating material is liable to cause water inside to condense, with the resultant reduction in its heat insulating efficiency. Crosslinked PE foam is, especially suitable as heat insulating material for low temperature applications such as for freezing room because it absorbs very little water.

Further, the excellent weatherproofness of this material makes it usable outdoors; for instance, for hothouse and sky house.

As it is soft to touch, it has now come to be used for warm clothes.

D. Buoy

Crosslinked PE foam has a high buoyancy, little water absorption, and good weatherproofness, and therefore makes an excellent buoy.

The conventional rubber buoy for fishing is now gradually being replaced by PE foam.

E. Packing material and core material

Owing to its proper elasticity and little water absorption, crosslinked PE foam is used as packing, sealing, gasket, etc., and also as a substitute of cork. High-density crosslinked PE foam is now used as core material of footwear.

5. Foamed polyethylene in Japan

Japan has only a short history of foamed polyethylene. High-density polyethylene foam other than the one for electrical cable covering was put on the market in 1962 for the first time in Japan, and low-density polyethylene foam production started in 1965. Now, after only two years since then, as many as nine makers manufacture foamed polyethylene and are developing its market. In concluding my speech, I should like to introduce to you the situation of the Japanese foamed polyethylene industry and some other information.

A. Foamed polyethylene makers.

Table 2 shows the Japanese foamed polyethylene makers. The total capacity of the nine makers listed is about 6,000 tons a year. (For your information, the polyethylene output in Japan for 1966 is 550,000 tons.) Their present operating rate is estimated about half their full capacity. Most of their products are in the form of sheet and slab.

The low-density foamed polyethylene makers have each a producing capacity of about 30 tons a month, still at the stage of pilot plant. But they have established an organization similar to makers association, and it is most likely that they will enter into full-scale production. At present there is no keen competition among them.

B. Uses and demand.

Foamed PE has the following outstanding characteristics, as compared with chief foamed products of polyurethane foam, polystyrene foam and foamed PVC. (Table 3)

Foamed PE is soft and strong and has a good shock-absorbing property and little water absorption and also a high resistance against chemicals. Crosslinked PE foam has an excellent weather-

proofness. It has better waterproofness, chemical-proofness, and compression strength than soft urethane foam and better flexibility, chemical-proofness, weatherproofness, and cushioning property than foamed polystyrene. It is superior to soft PVC foam in stability in size, chemicalproofness and weatherproofness.

Before, I have introduced some applications of foamed polyethylene. Since many kinds of foamed polyethylene with different shapes, specific gravities, and cell structures are manufactured, they are used for a great variety of applications. As many outstanding features of foamed polyethylene are now recognized as I said before, it is increasingly in demand in various industries, despite its high cost.

Because of its short history in Japan, it is difficult to estimate future demand for foamed polyethylene in our country. Some estimates agree in one point that demand for foamed polyethylene will make a sharp increase in a few years to come. A recent estimate forecasts the future demand as shown in Table 4. Fig. 14 shows a comparison with the estimated future demand for other foamed materials. It is expected to find a great demand in such industries as of cushion material, packing material, building material, vehicles stock, and so on.

C. Cost

The cost of foamed polyethylene varies with its density and the shape of its product; but is higher than that of urethane or polystyrene foam now. The prices of foams in Japan are shown in Table 5. Although it is difficult to estimate the trend of the price in future, it is expected that when the producing capacity reaches about 1,000 tons per month, foamed polyethylene will be able to compete with foamed polystyrene.

D. Evaluation and future of foamed polyethylene

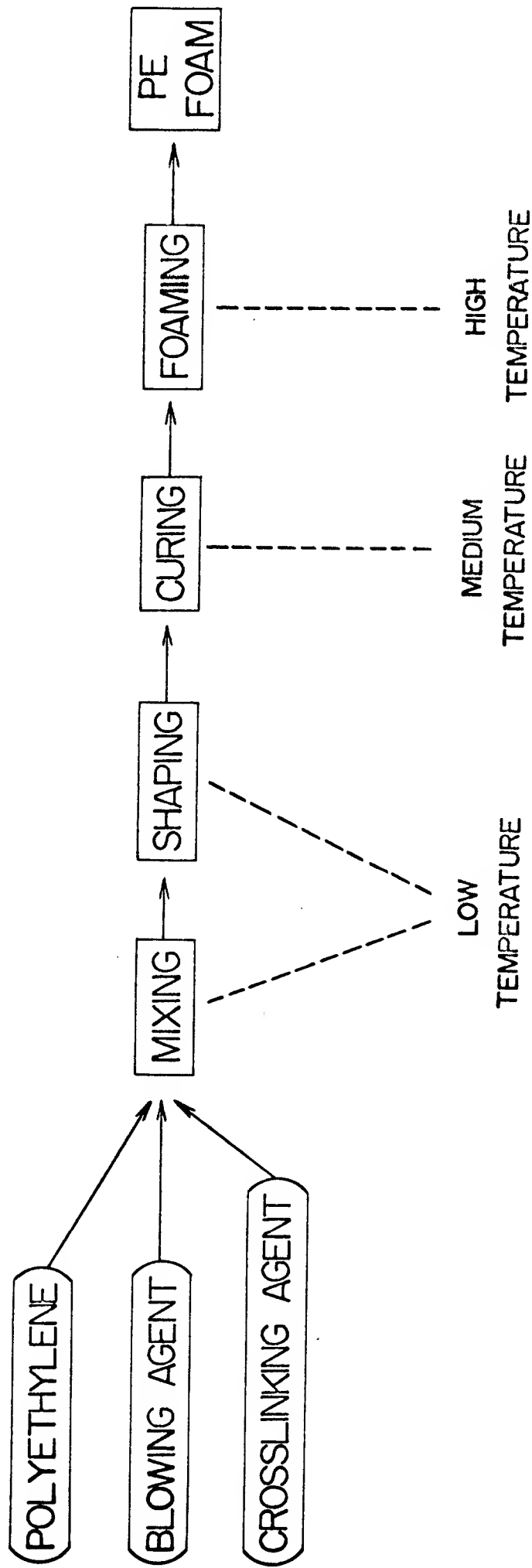
Because it has superior properties, foamed polyethylene is now gradually replacing urethane or polystyrene foam and natural materials. But, there have not so far been found many applications where foamed polyethylene is a vital requirement. There are also some problems yet to be solved, including cost reduction, flame retardancy, manufacture of thick foam, prevention of electrostatic charge build-up, realization of gas transmission, improvement of processing techniques, and so on.

It is generally believed, however, that foamed polyethylene is not a "special" but "excellent" foam. It is therefore expected that foamed polyethylene, because of its superior properties, will find much demand in future as the third foam for all purposes, in competition with polyurethane and polystyrene foams. It will be extensively used not only as material to fill any space but also as a foam to make the most of its outstanding features.

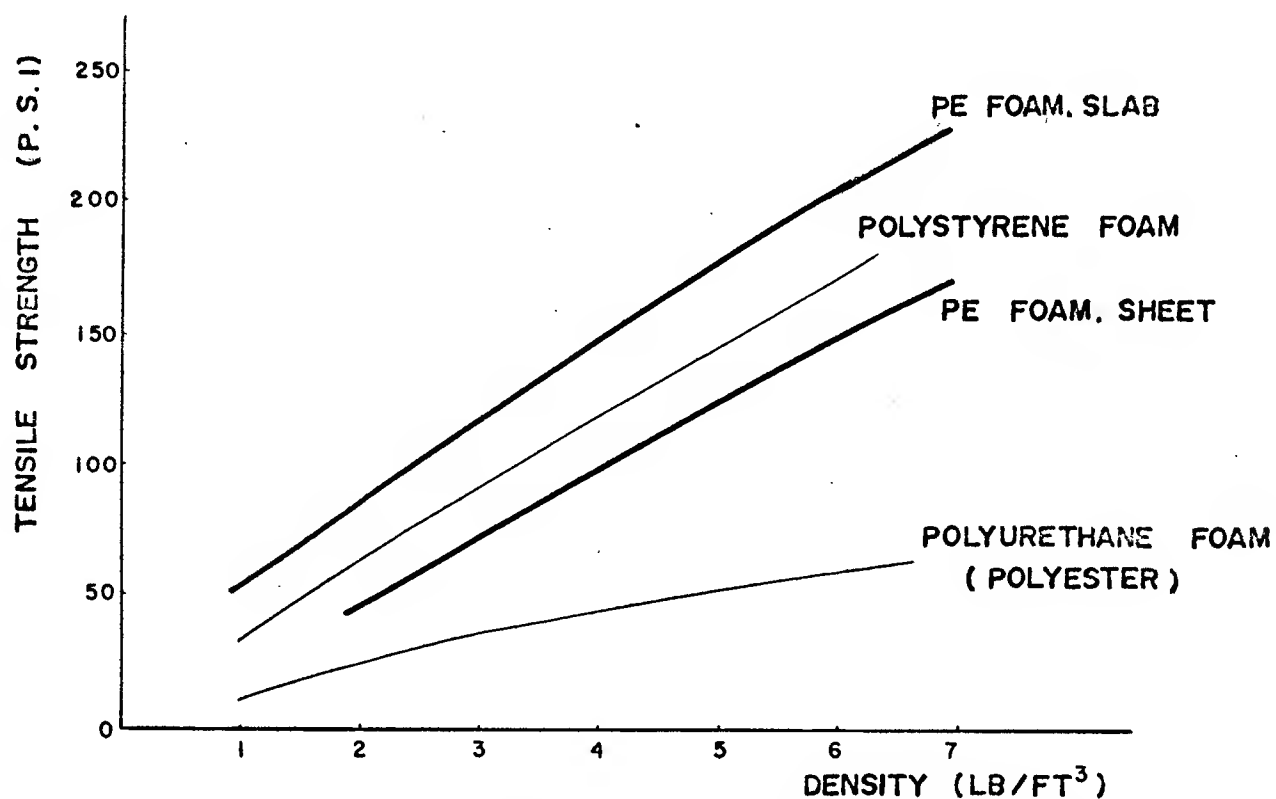
Reference

- 1) Japanese Patent Application No.42-2278 (Nippon Kakō Seishi)
- 2) U.S.P. No. 3,067,147 (The Dow Chemical Co.)
- 3) U.S.P. No. 2,256,483 (E.I. du Pont de Nemours Co., Inc.)
- 4) Henry R. Lasman, SPE Journal, 1184 (Sept. 1962)

FIG. 1 PROCESS DIAGRAM OF CHEMICALLY - CROSSLINKED PE FOAM



FIG,2 DENSITY VS. TENSILE STRENGTH



FIG,3 DENSITY VS. BREAK ELONGATION

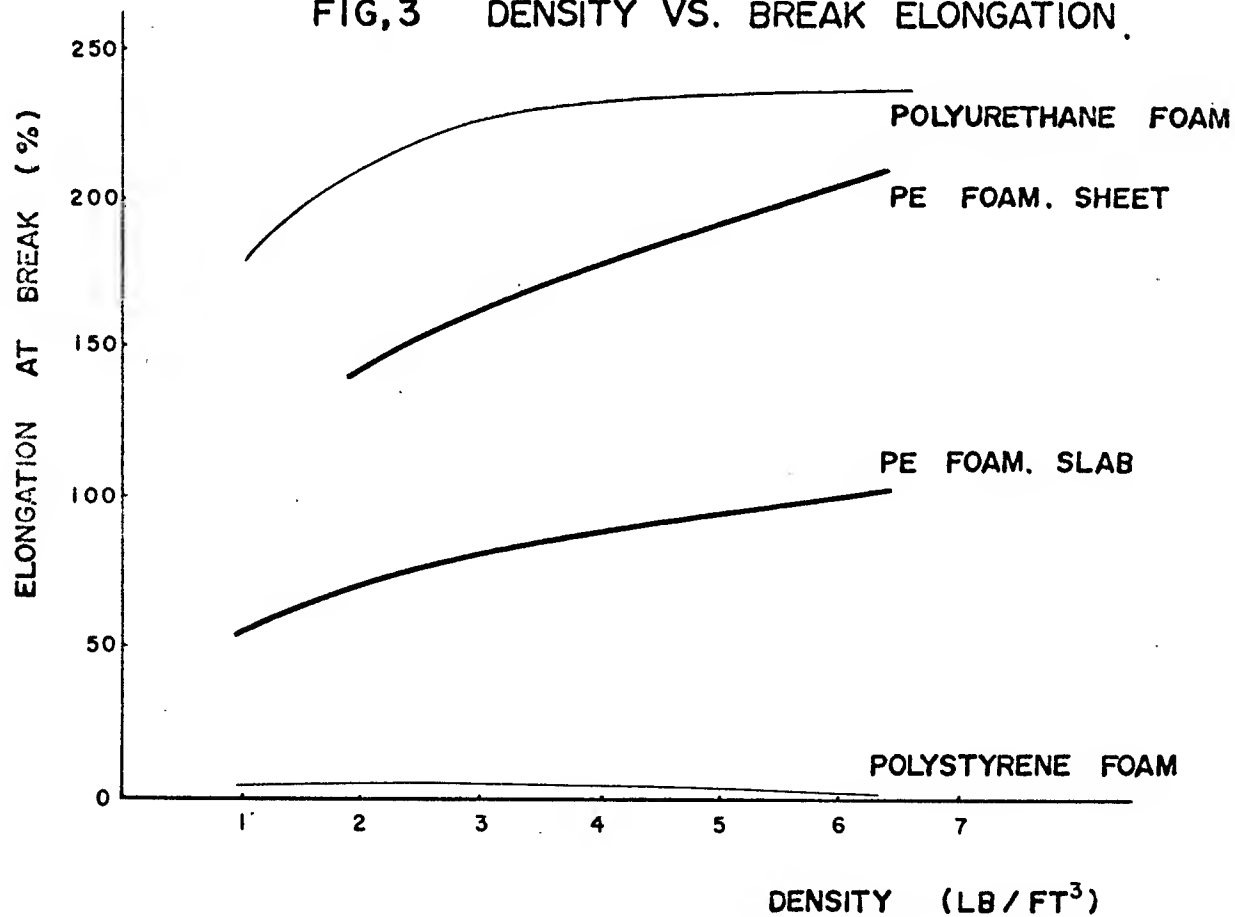


FIG. 4 DENSITY VS. COMPRESSIVE STRENGTH.

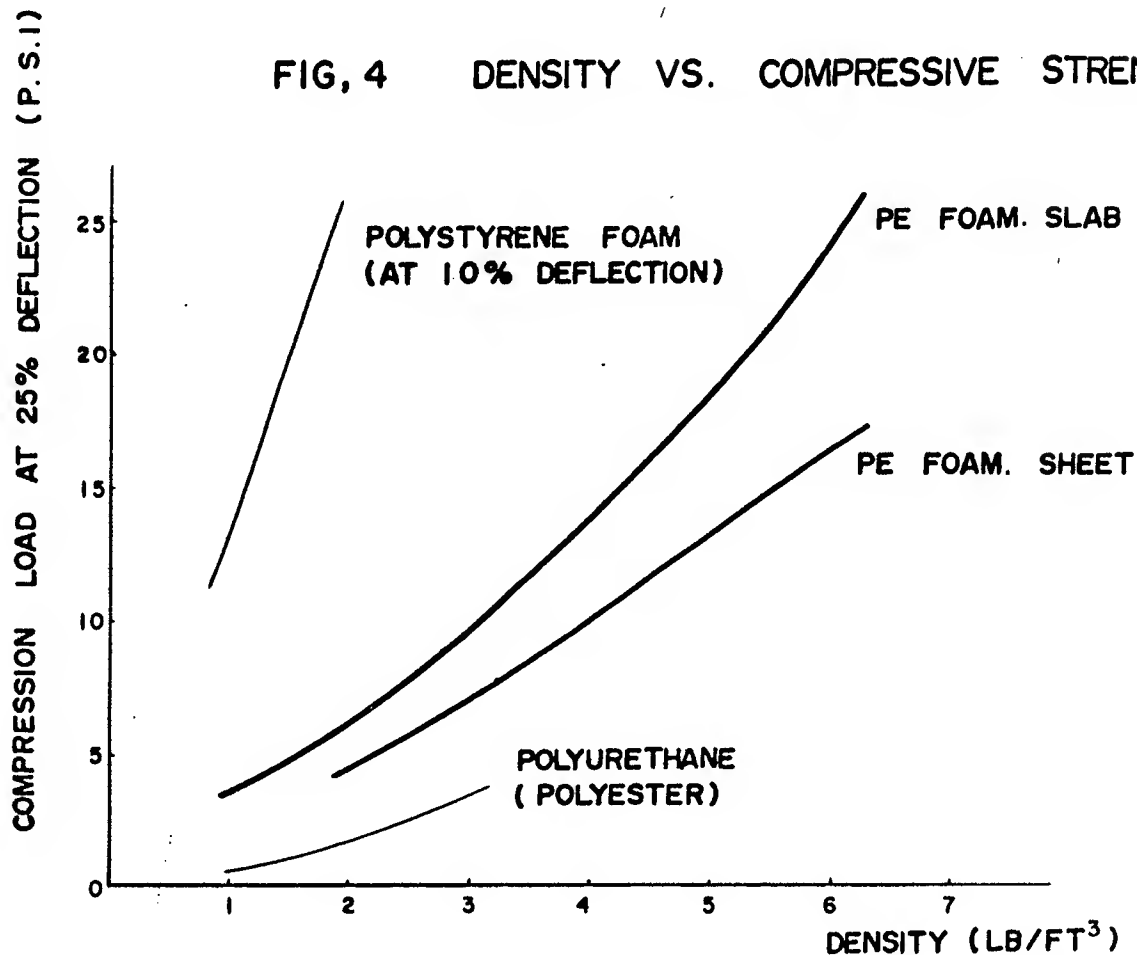


FIG. 5 COMPRESSION DEFLECTION OF FOAMS.

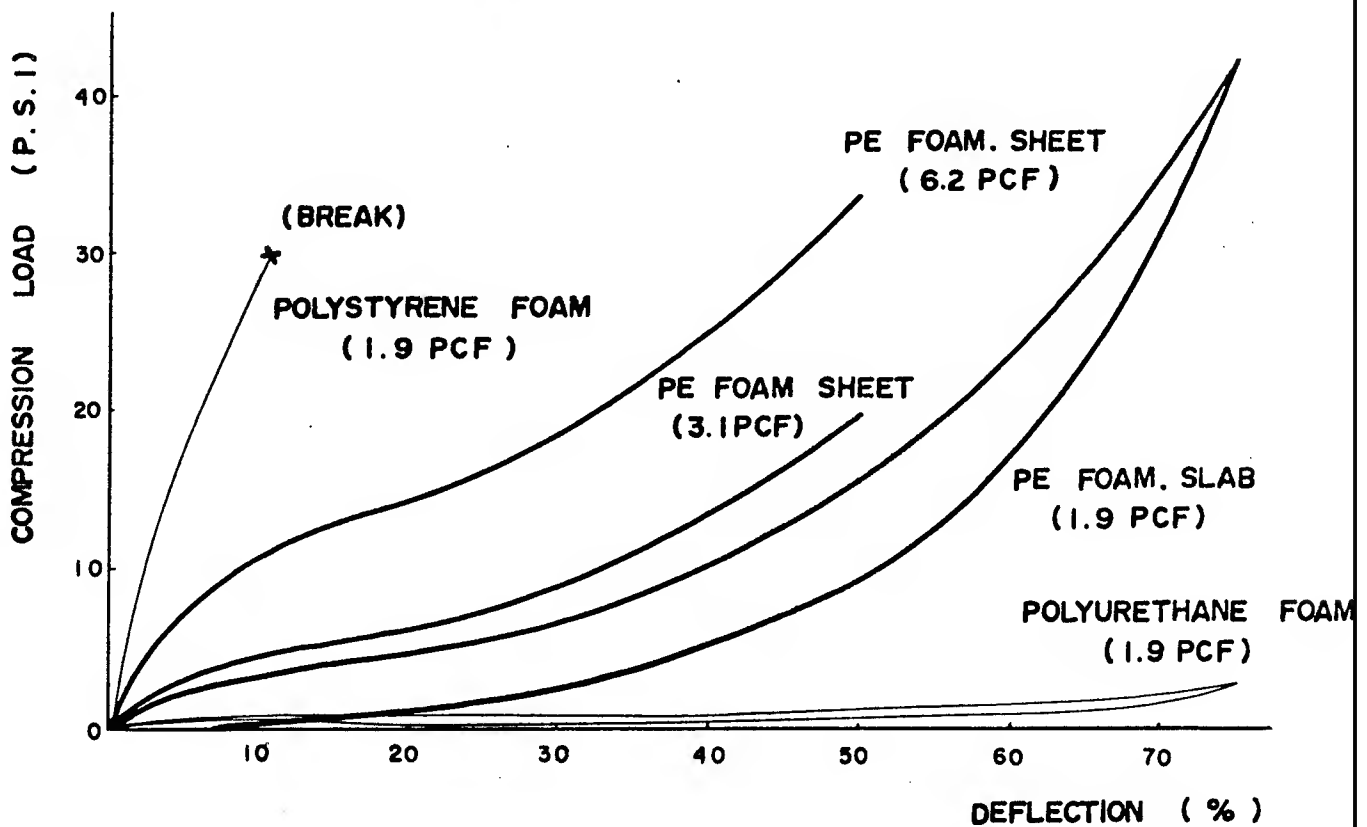


FIG.6 DENSITY VS. COMPRESSION SET.

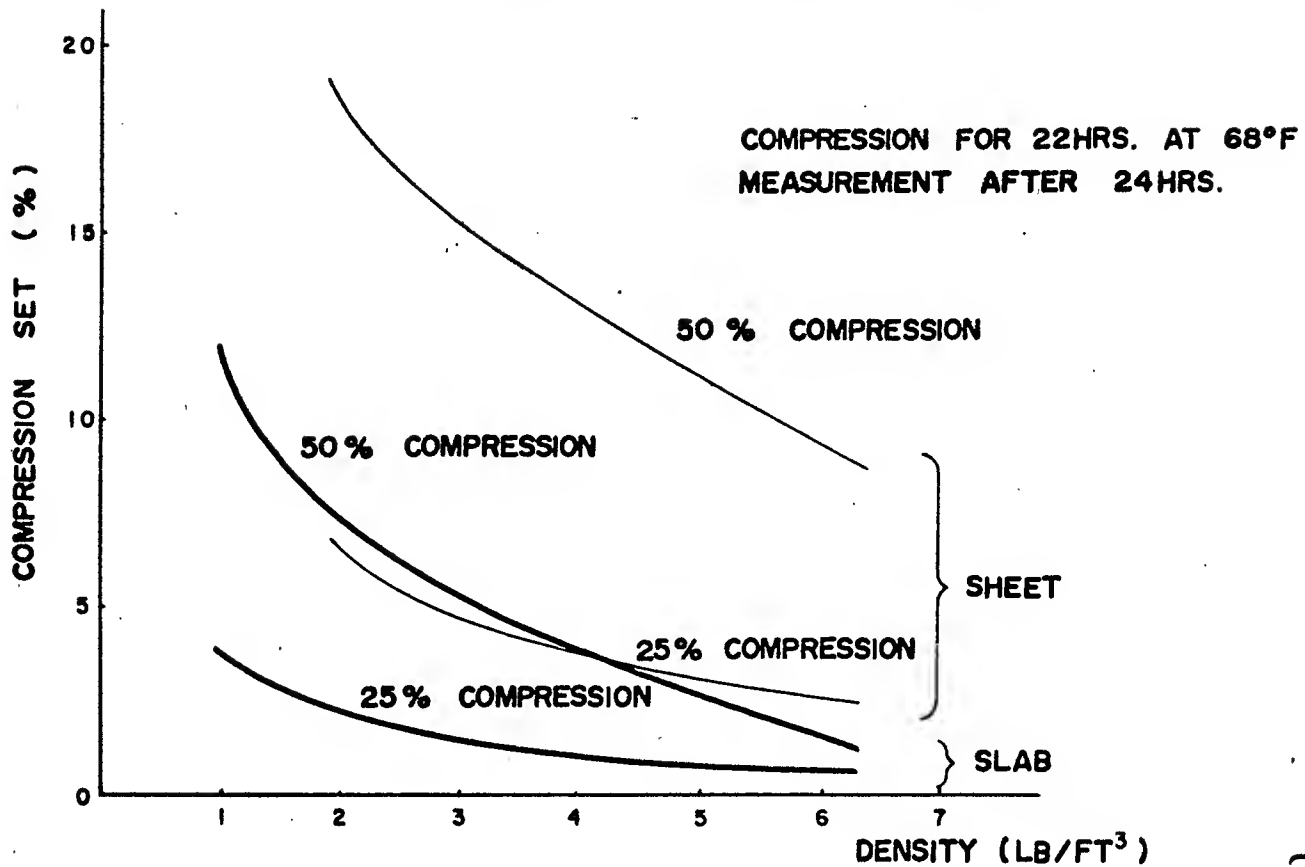


FIG.7 REPEATING COMPRESSION PROPERTIES.

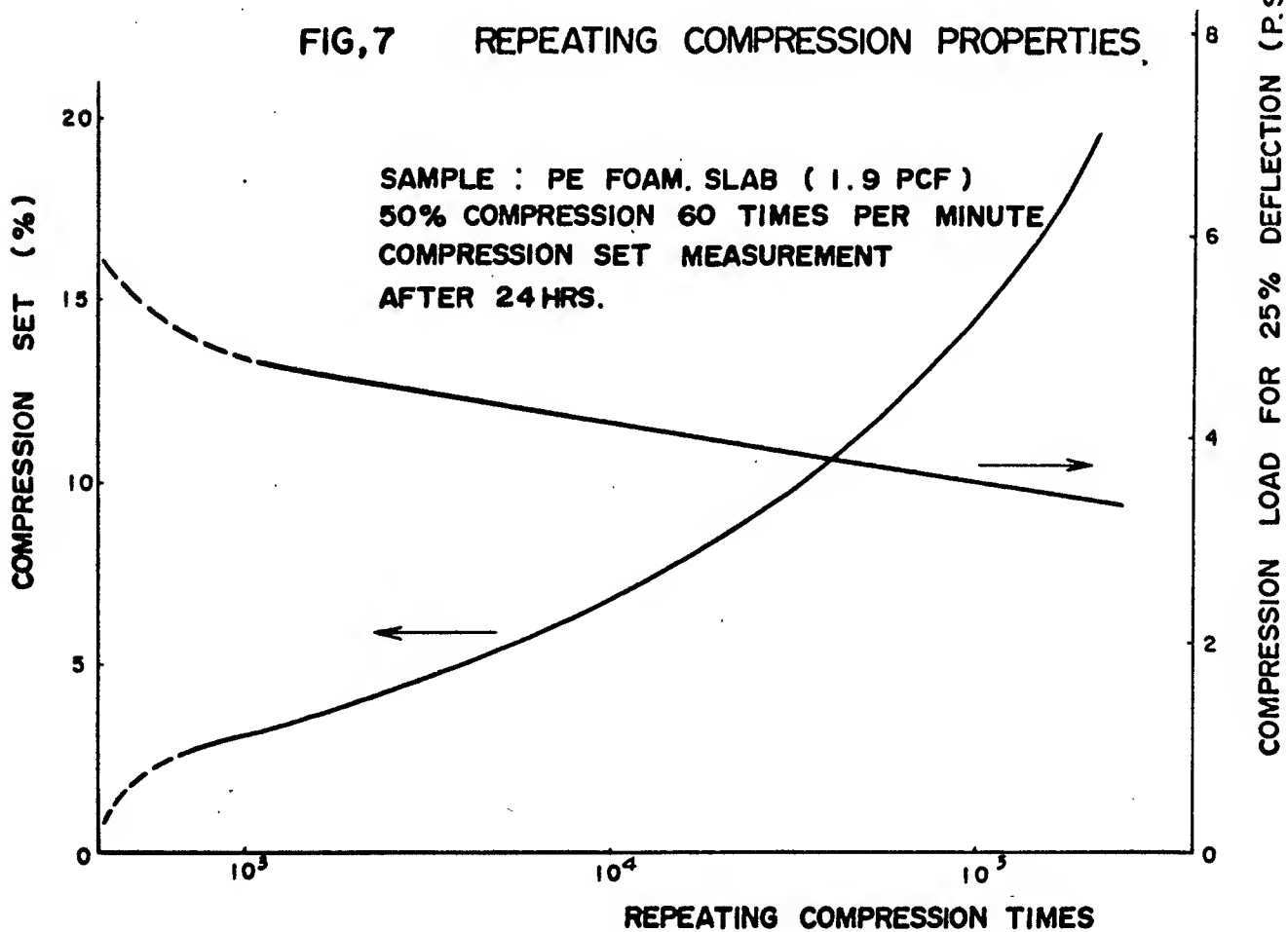
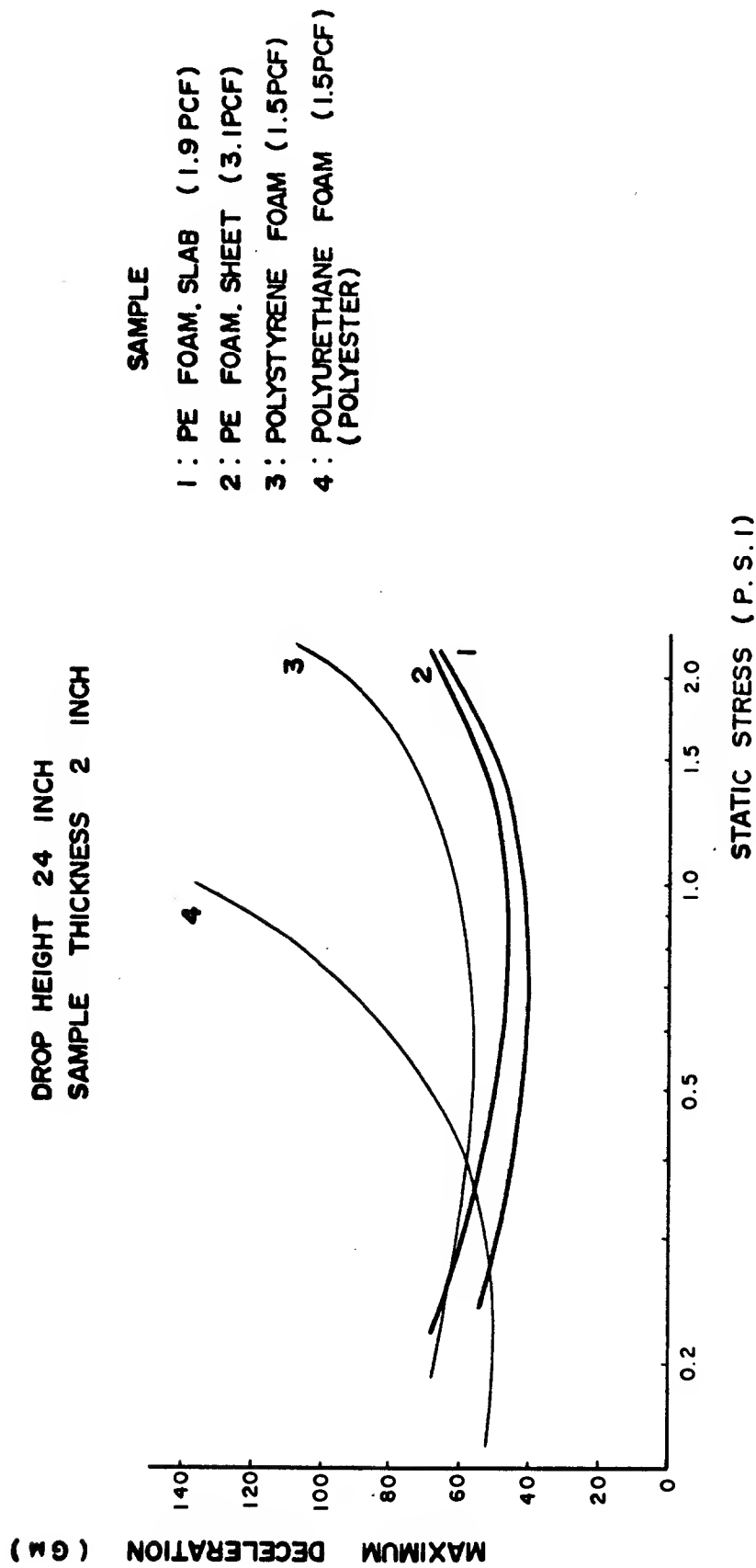
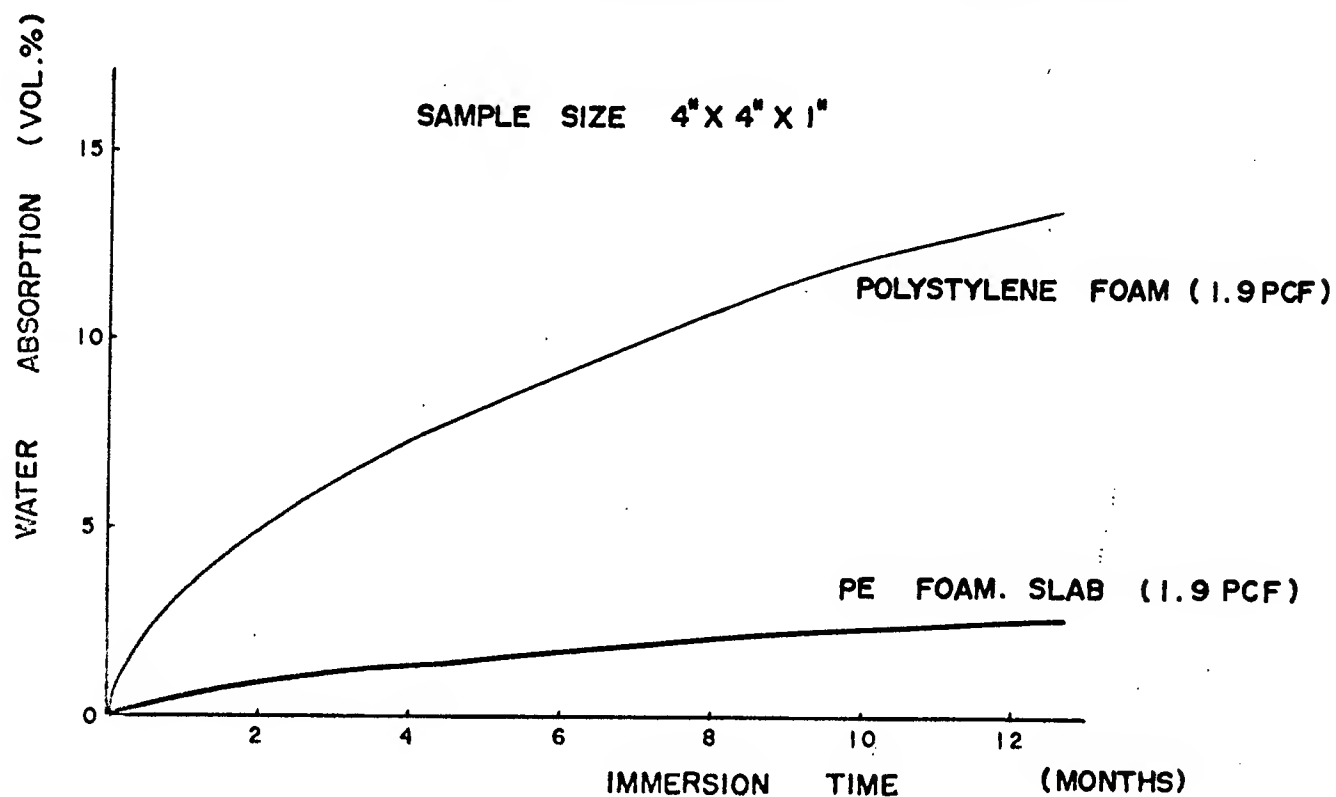


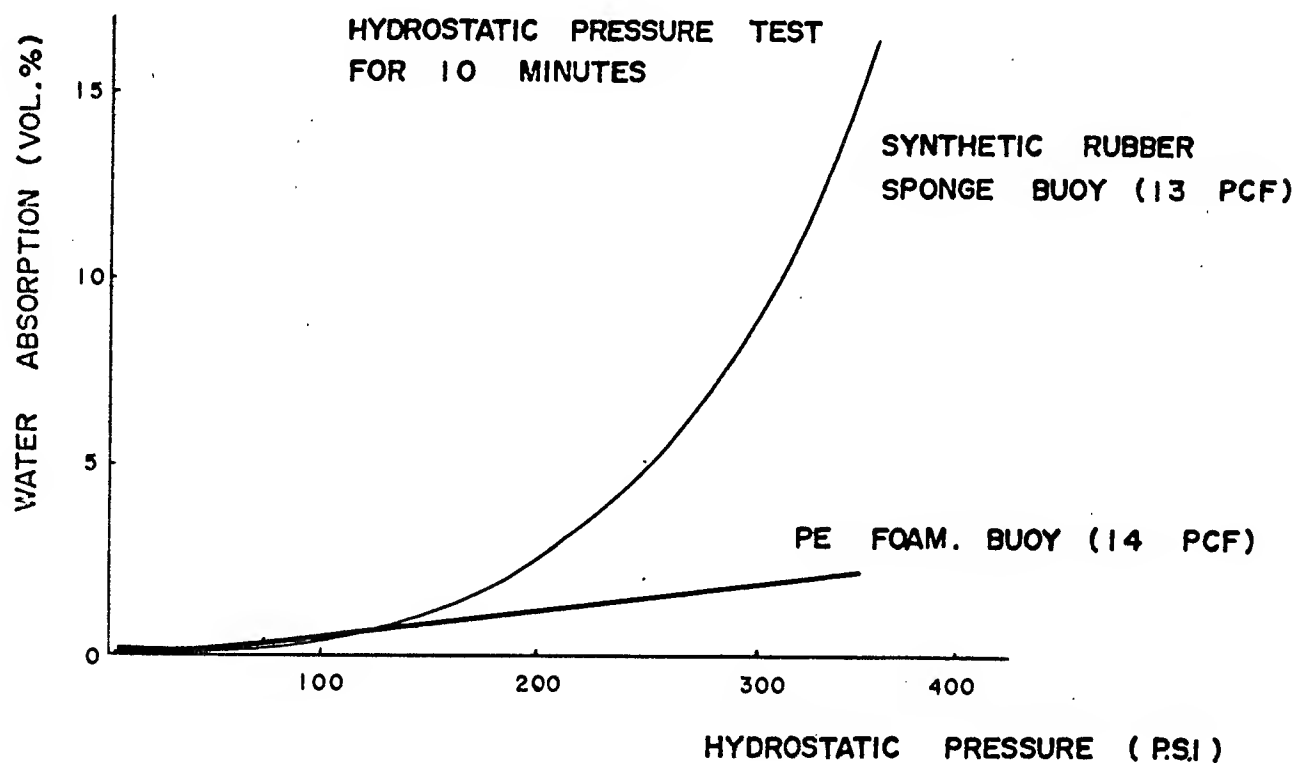
FIG.8 DYNAMIC CUSHIONING DATA.



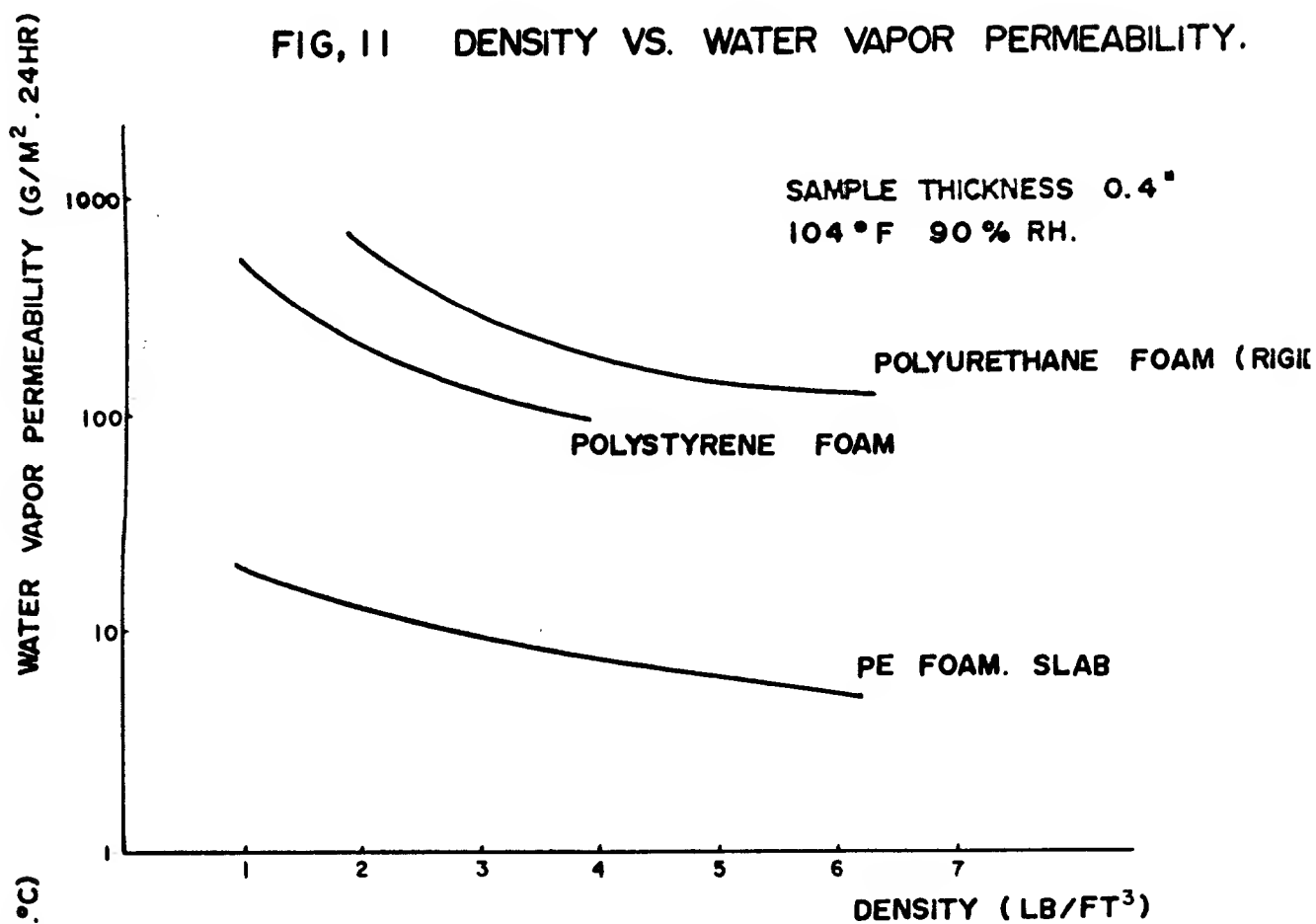
FIG,9 WATER ABSORPTION BY IMMERSION TEST.



FIG,10 WATER ABSORPTION UNDER PRESURE.



FIG,11 DENSITY VS. WATER VAPOR PERMEABILITY.



FIG,12 DENSITY VS. THERMAL CONDUCTIVITY.

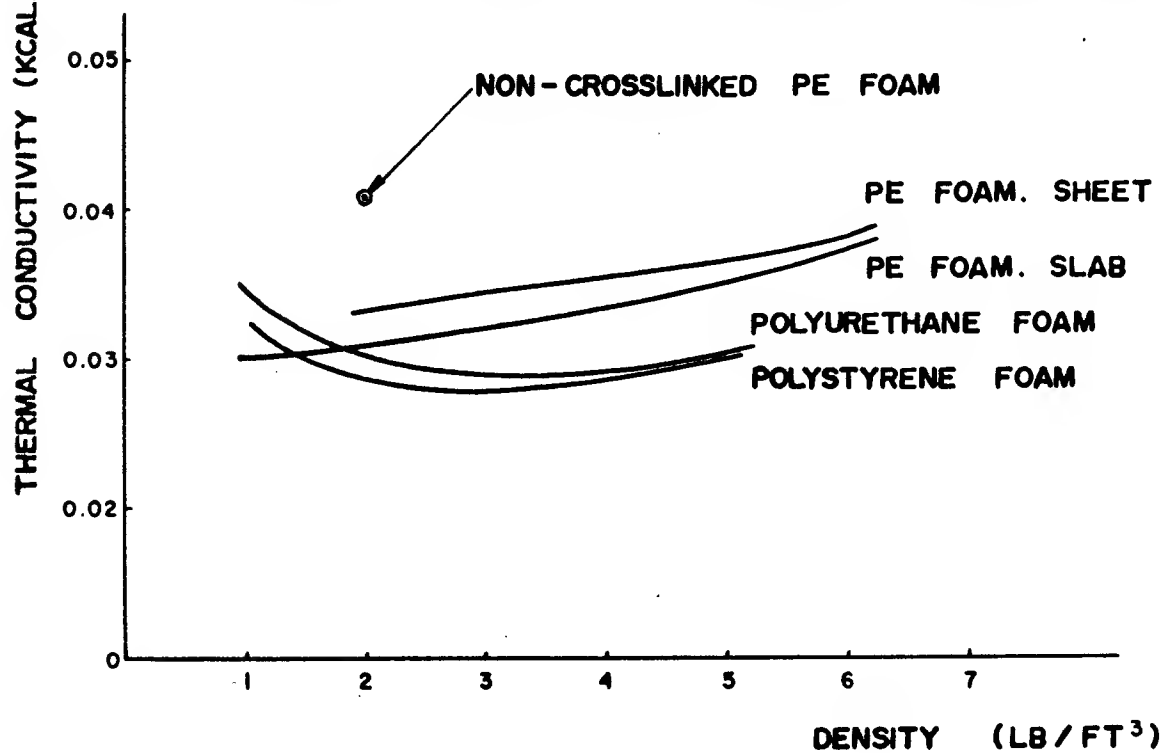
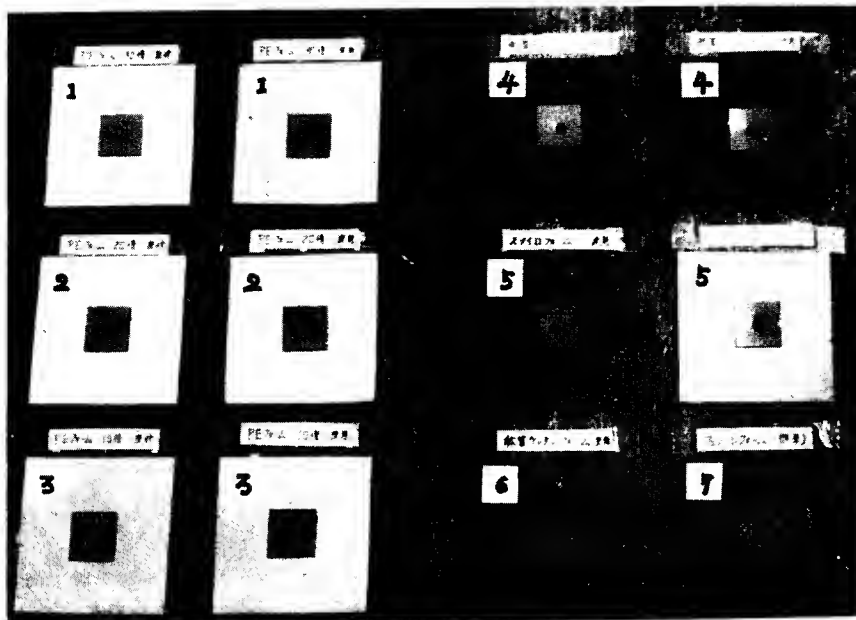
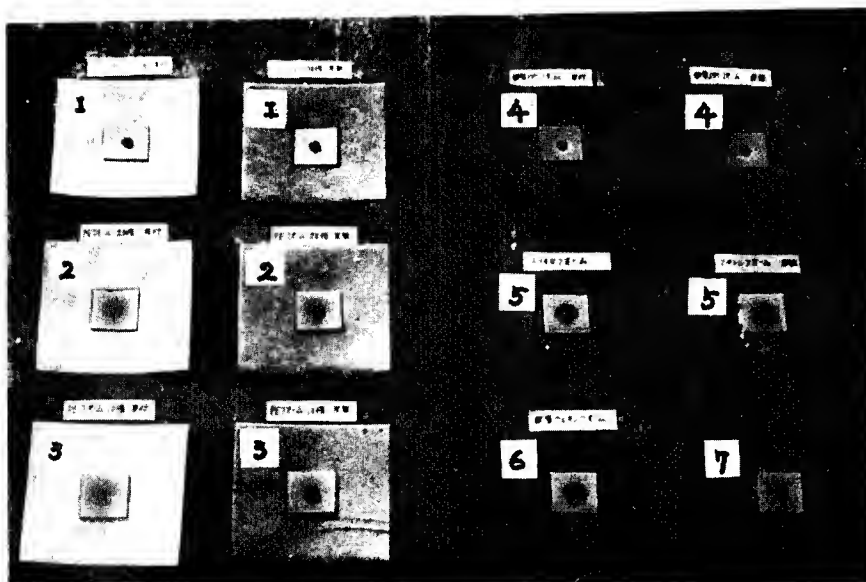


Fig. 13 Weathering Test of Foams



(Before exposure)



(After 1 year's exposure)

- Sample 1: Chemically Crosslinked PE Foam (1.9 pcf)
 2: Chemically Crosslinked PE Foam (3.1 pcf)
 3: Chemically Crosslinked PE Foam (6.2 pcf)
 4: Flexible PVC Foam
 5: Polystyrene Foam
 6: Polyurethane Foam
 7: Phenolic Foam

FIG.14 MARKET ESTIMATION OF CELLULAR MATERIALS
IN JAPAN.

(FOR 1965 SOURCE..... JAPANESE FOAM
'INDUSTRIES' ASSOCIATION.)

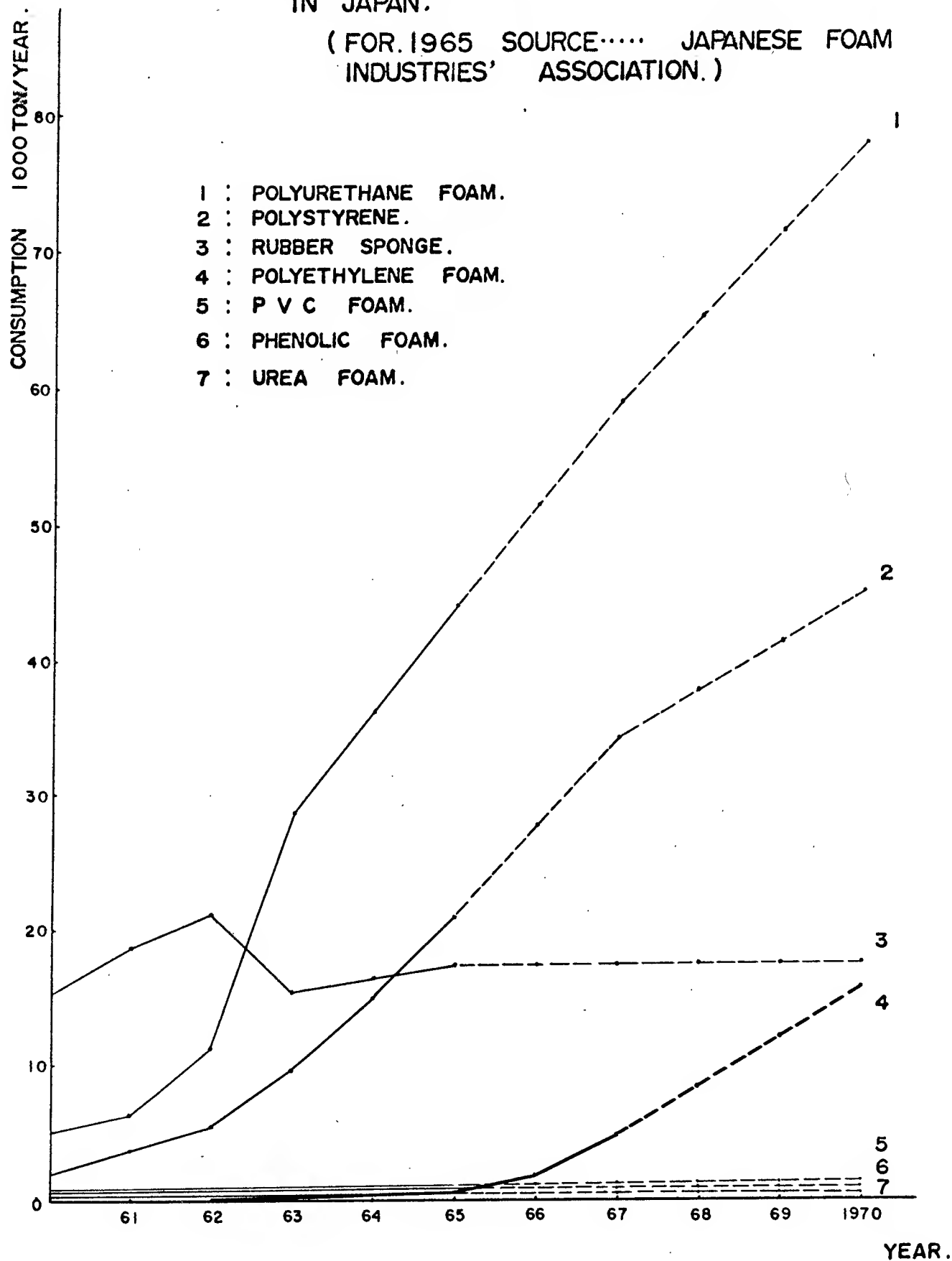


Table 1 Weather-o-meter Test of Foamed Materials

Foams	Crosslinked PE Foam	Polyurethane Foam	Polystyrene Foam	PVC Foam
Color	No change	Discolored	No change	Discolored
Form	No change	No change	No change	Distorted
Surface	No change	Hardened	Eroded	Hardened
Weight loss (100 hrs) (200 hrs)	0.3% 0.9%	0.6% 1.5%	0.4% 4.4%	4.8% 7.8%
Shrinkage (100 hrs) (200 hrs)	< 1 % < 1 %	< 1 % < 1 %	< 1 % < 1 %	11 % 17 %
Tensile strength (100 hrs) (200 hrs)	94 % 90 %	73 % 49 %	90 % 50 %	120 % 93 %
Elongation change (100 hrs) (200 hrs)	100 % 96 %	81 % 64 %	Unmeasurable	88 % 77 %

Table 2 Polyethylene Foam Production in Japan

Manufacturer	Start year	Capacity t/m	Product		Process	
			Form	Density (pcf)	Crosslinking	System
Maruto Chemical Co.	1962	100	Sheet	High 29-37	None	Continuous
Nippon Kakō Seishi Co.	1965	100	Film & bottle	High 24-29	None	Continuous
Eiwa Chemical Ind.	1965	35	Slab	Low- medium 3.7-13	Chemically	Batch
Sekisui Chemical Co.	1965	30	Sheet	Low 2.1-6.3	Irradiation	Continuous
Hitachi Chemical Co.	1965	30	Sheet	Low 2.5-6.3	Chemically	Continuous
Asahi Dow Co.	1965	-	Slab & rod	Low 2.1	None	Continuous
Toyō Rayon Co.	1965	30	Sheet	Low 2.3-6.5	Irradiation	Continuous
M.T.F. Chemical Co.	1966	20	Slab	Low 2.5-5.0	Chemically	Batch
The Furukawa Electric Co.	1966	50	Slab	Low (1.2)-1.9	Chemically	Batch
			Sheet	Low 3.1-6.3	Chemically	Continuous
			Shaped product	Medium 5 - 20	Chemically	Batch

Table 3 Comparison of Properties of Foamed Materials

Foam	Chemically- crosslinked polyethylene	Polyurethane		Polystyrene	FVC (Flexible)
		(Flexible)	(Rigid)		
Density (pcf)	> 1.2	> 0.9	> 2	> 0.9	> 3.1
Cell structure	Closed	Open	Closed	Closed	Open-closed
Mechanical property	Large	Small	Medium	Fragile	Medium-small
Hardness	Fairy hard	Soft	Fairy hard	Hard	Medium-soft
Water absorption	Extremely small	Very large	Small	Small	Small-large
Durability against chemicals	Very good	Good	Good	Unsatisfactory	Unsatisfactory
Weather proofness	Very good	Unsatisfactory	Unsatisfactory	Unsatisfactory	Unsatisfactory
Maximum service temperature (°F)	170	210	210	160	140
Combustibility	Combustible	Combustible (Poisonous gas)	Combustible (Poisonous gas)	Combustible (Black smoke)	Self- extinguishing (Poisonous gas)
Cushioning property	Excellent	Good	Good	Fair	Good

Table 4 Estimated Demand for
PE Foam in Japan

(Unit: Ton)

Uses \ Year	1965	1966	1967	1968	1969	1970
Packaging material	70	290	850	1,900	2,650	3,150
Building material	10	70	190	350	490	600
Vehicles	10	200	750	1,300	1,900	2,500
General industries	50	500	1,000	2,000	3,000	4,000
Disc packing	20	50	300	700	1,000	1,300
Footwear	15	70	200	400	550	650
Clothes	5	30	80	150	250	300
Mattress	0	10	30	50	80	100
Blow bottle	10	30	50	100	130	150
Electric wires and cables	50	100	150	200	250	300
Agriculture	50	100	200	250	300	350
Sundry goods and others	100	250	700	1,300	1,800	2,200
Total	390	1,700	4,500	8,700	12,400	15,600
PE Out put (1,000 t)	380	470	530	610	690	820
PE Foam/PE (%)	0.10	0.36	0.85	1.4	1.8	1.9

Source: Japanese PE Foam Manufacturer's Association

Table 5 Cost of Foamed Materials in Japan

	Density lb/ft ³	Cost per Volume ¢/ft ³
Polyethylene Foam		
Sheet, high density	24 - 37	156 - 270
Sheet, low density	2.1-6.5	27 - 66
Slab, low density	1.9-6.9	31 - 60
Polyurethane Foam		
Rigid type	2.0-2.3	16 - 23
Flexible type	< 1.2	12
Polystyrene Foam		
Sheet, high density	6.2	31 - 47
Block, low density	1.2-1.9	12 - 16
PVC Foam		
Rigid type	3.7	39
Flexible type	5.0	31
Rubber Sponge		
Rigid type	6.2	20 - 39
Soft type	4.4	31

4-25-67 10 21 4-11

Dielectric Strength of Rigid Urethane Foam*

by

J. Moacanin, J. Farrar, and I. N. Einhorn**

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

1. Introduction

Cellular plastics are attractive as dielectric materials for space applications because of their low dielectric constant and loss factor, low weight-to-strength ratio, RF transparency, and impact protection. For future space missions there is need for components which will operate reliably over periods of up to several years in the rigor of the space environment. A survey of the literature disclosed that very little meaningful information is available on the various parameters pertaining to the electrical properties of foams. This lack of information dictated the exclusion of foams from JPL specifications for high-voltage packaging (Ref. 1), and created the need for a systematic and comprehensive study. Although the work was motivated mainly by spacecraft problems, we were forced by necessity to take a broader approach.

For high-voltage space applications conditions conducive to electric failure occur when one operates at reduced pressure, i.e., when the gas pressure is in the "critical region" in which the gas will support corona

* This paper represents one phase of research performed by the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration, Contract NAS7-100.

** Wayne State University, Detroit, Michigan

or arcing. Such conditions exist in terms of Earth altitude between 60,000 and 310,000 ft. It is believed that the failure of the TV cameras on Mariner IV was due to arcing caused by an accidental power turn-on during ascent through the upper atmosphere. Corona problems are encountered with antennas of high flying airplanes. For the Voyager lander an antenna will have to be encapsulated for impact protection and for operation in the low atmospheric pressure on the surface of Mars (10 to 50 mm Hg) (Ref. 2). In deep space, i.e., vacuum of less than 10^{-5} mm Hg, occurrence of gas supported discharge is not possible, but problems can be caused by inadequately ventilated areas such as voids around connectors (Ref. 3).

The relationship between the breakdown voltage and the product of the pressure, P , times the separation, δ , between two parallel plates (Fig. 1-1) is given by Paschen's law which was discovered experimentally in 1889. For any give $P \delta$ product there is a breakdown voltage, where an arc occurs. Fig. 1-2a shows that Paschen's minimum occurs at about 330 V, which means that any voltage under 330 V would not arc over regardless of air pressure or geometry. The breakdown of solid dielectrics is caused quite commonly by discharges in gases in flaws or voids; but other mechanisms are possible as discussed below. Although a foamed plastic can be viewed as a composite of a polymer and a gas, its breakdown behavior cannot be predicted by interpolating between solid and gas behavior.

The purpose of this paper is to discuss the effect of the following parameters on the electrical properties of cellular plastics: (1) chemical composition of both gas and polymer, (2) density, (3) cell size, structure and orientation. The main emphasis is on the dielectric breakdown--the principal area of our work to date--but some aspects of dielec-

tric properties and corona are also included. A detailed analysis of gas diffusion in a closed cell foam was presented in the literature (Ref. 4).

2. Test Methods

Dielectric strength or electric breakdown of plastics is defined as the point at which voltage can no longer be maintained across the material without excessive flow of current or the physical disruption of the material. Several types of electric breakdown can be recognized in solids: intrinsic breakdown, physical defect dependent breakdown, thermal breakdown, and discharge-dependent breakdown. It is important to recognize the existence of the different types of breakdown, since different conditions and material characteristics may emphasize different modes of failure (Ref. 5). But for cellular materials the discharge dependent breakdown is without much doubt the major cause of breakdown as discussed below.

The voltage stress gradient, E , across a uniform sample is defined by:

$$E = V/t$$

where V is the voltage, and t the specimen thickness. The voltage gradient at failure is defined as breakdown stress, breakdown strength, electric strength, or dielectric strength. A flashover is a failure which may occur around the end of a sample instead of through its volume and, in general, is not considered a property of the material.

A detailed description of experimental requirements and specifications of test conditions are given in ASTM D149-61 "Standard Methods of Test for Dielectric Breakdown Voltage and Dielectric Strength of Electrical

Insulating Materials at Commercial Power Frequencies." These cover procedures for testing solid, semisolid, and liquid electrical insulating materials, and are also applicable to cellular plastics.

For this study measurements were made with a Dielectric Strength Test Set, Model PDA-1, (Industrial Instruments Inc.) using the 60 cy. mode. This tester meets ASTM specifications. Fig. 2-1 shows a foam specimen in the test compartment. Cylindrical brass electrodes $1/4$ " with rounded edges were used. To ascertain the stability of the tester the breakdown voltage of air was checked periodically; the breakdown voltage for a 1" air gap was 17 ± 1 KV. The foam specimen size was at least 4" x 4" in order to avoid flashover. The thickness varied between 0.25 - 1.00 in; the optimum value was dictated by the 50 KV_{rms} limit of the instrument.

3. Experiments and Results

3.1 Water Blown Urethane Foam

The initial phase of this study was carried out on Eccofoam S and SH (Emerson and Cuming, Inc.) water blown rigid closed-cell urethane foams. They are distributed as 1" thick sheet stock; the density ranged between 2 and 26 lb/ft³. According to the manufacturer Eccofoam S can be used between -70 and 150°C without physical deterioration; SH is the high temperature foam and its limit is 204°C.

Effect of density and blowing gas pressure. Tests were carried out on specimens as received. For each density, five breakdown tests were made, and the length of the vertical line indicates the spread of the data points. For the 2 lb/ft³ specimen, however, 25 tests were made with no apparent

increase in the spread of data points, indicating that 5 tests yield a reasonable estimate of the statistical deviation for this test procedure. Additional tests were carried out on specimens which were outgassed at 80°C in a vacuum of 1 mm Hg. In this context outgassing is the outward permeation of volatile components from a foam placed in vacuum. The specimens were allowed to cool to ambient temperature under vacuum before removal for testing. This procedure minimized back diffusion of gases into the foam (Ref. 4). The actual core density of the test specimens was determined by weighing a 2 inch cube.

Inspection of Fig. 3-1 shows that the breakdown voltage E_b , for the 2 lb/ft³ foam is 25 kv as compared to 17 for air at 1 atm. This increases further to about 38 kv for the 8 lb/ft³ specimen. For specimens outgassed for 6 days a reduction of about 8 kv is observed, and an additional loss of 5 kv for those outgassed for 37 days.

The actual pressure of the blowing as in the outgassed specimens was not determined, but reasonable estimates may be made on the basis of previous studies on the outgassing behavior of foams (Ref. 4). After 6 days at 80°C one should expect a loss of approximately 90% of the blowing gas leaving the remaining as at an average pressure of about 60 mm Hg. After 37 days about 99% of the gas should be removed, and the pressure should be about 5 mm Hg. Inasmuch as only about 1% of the gas is left after 37 days, it appears that during this period the asymptotic value for the strength of the foam has been approached. For comparison, Fig. 3-2 shows the change of voltage with pressure for CO_2 and N_2 .

Dependence of E_b on rate of voltage application. To assess the effect of the rate of voltage application on E_b , a series of tests were carried out

on a 2 lb/ft³ Eccofoam SH. By varying the rate, the time to breakdown could be increased from the usual 30 to 60 sec. for short time tests to 2 to 3 hrs. The results are shown in Fig. 3-3.

Dependence of E_b on thickness. For this study sheets of 2.5 and 6 lb/cu ft Eccofoam SH, were used. Thickness was varied from approximately 0.15" to 2".

The test results for both foam densities are shown in Fig. 3-4 as plots of $\log V_b$ versus $\log t$, where V is the voltage at breakdown and l is the specimen thickness. These plots yield good straight lines. The slope for the 2.5 lb/ft³ foam is about 0.6, and that for the 6 lb/ft³ about 0.5. These results show that in this respect a foam behaves like a solid. The slope for the 2.5 lb/ft³ foam is only slightly higher than 0.5, a value which is also characteristic of a solid. Inasmuch as a density of 1.8 lb/ft³ is the practical lower limit for rigid urethane foams, one concludes that the 0.5 value should represent the behavior of foams of all densities of interest.

3.2 Flexible Foam

Seven flexible foams were received from Scott Paper Company (through the courtesy of Dr. E. A. Blair). The cell size varied by a factor of ten; the content of broken cell windows was high in all samples. The results are tabulated in Table 1.

3.3 Fluorocarbon Blown Foam

All the fluorocarbon blown foams were prepared at Wayne State University, using a Martin-Sweets Company laboratory model foam machine. The foaming apparatus consists of a three component positive displacement

metering and mixing machine having a maximum capacity of 2 lb/min. Core samples selected for testing were cut out from buns approximately 4" x 9" x 4".

Effect of polymer composition on breakdown. A series of foams varying in composition have been prepared (Table 2). These samples were tested without regard to the direction of foam rise. It was near the end of the measurements that we discovered the strong directional effects. For all subsequent tests the orientation of the test specimen was recorded. Because of the neglect of directional effects, the comparison of these results in terms of effect of formulation on E_b are inconclusive, although it appears that increasing the crosslinking density in the polymer increases E_b (formulations 3057 and 3024). This problem did not arise with Eccofoam specimens; they were furnished as 1" thick slabs, and thus by necessity were tested only in the direction of foam rise.

Effect of density and cell size. Two representative formulations were selected from Table 2; these were 3111-5 (low crosslink) and 3024-17-35 (high crosslink). For each of these the fluorocarbon content was varied in order to vary density. In addition, the longest dimension of the foam cell was measured in each direction, i.e., with (||) and across (⊥) the direction of foam rise. The diameter of the strut was also recorded.

These measurements were made with a binocular microscope at 34x magnification (10x eyepiece, 3.4x objective). The eyepiece scale was calibrated with a reference slide (52 divisions = 1.0 mm).

Table 3 summarized results on formulation 3111-5 and Table 4 on formulation 3024-17-35. These data demonstrate the strong correlation between E_b and the cell dimension in direction of the electric field.

Currently we are carrying out a study of the correlation of cell structure with E_b . Figure 3-5 illustrates the variety of cells one encounters. It is apparent that features such as the distribution of polymer between struts and windows, uniformity in cell size and structural integrity of windows depend strongly on the formulation.

4. Discussion

4.1 Some Aspects of Dielectric Breakdown in Solids

From a cursory inspection of the results it becomes apparent that with respect to breakdown foams behave more like a solid than like a gas. For example, the breakdown strength, E_b (KV/in), varies as the square-root of the thickness (Fig. 3-4), in analogy to solids, whereas for a gas E_b is nearly constant. Furthermore, as the blowing gas is removed the decrease in E_b of the foam is considerably less than that for the pure gas. However, there is strong presumptive evidence that breakdown is discharge initiated. If intrinsic breakdown were important one would not expect E_b to be rate dependent (Fig. 3-3). In view of these observations it appears reasonable to formally consider a foam as a solid in which breakdown is controlled by discharges in voids or flaws. It is therefore appropriate to discuss some aspects of dielectric breakdown in solid insulators; (this part of the discussion follows closely Ref. 6).

It has become accepted in recent years that gaseous discharges frequently limit the application of many plastics with good dielectric properties. This type of breakdown is produced by electrical discharges occurring in gas-filled cavities in the body of the material, or at the edges of electrodes adjacent to the material. The cavities arise from imperfections in the manufacture of insulated components. As pointed out above E_b for a

gas does not depend on the thickness of the layer (Fig. 1-1). But when the layer becomes very thin E_b starts to increase, and for about 0.2 mils becomes comparable to that of a solid dielectric (Fig. 4-1). Thus, when an electric stress is applied to a solid having a gas filled space in series with it, local breakdown of the gas will occur before the solid dielectric is overstressed. For structures of this type (Fig. 4-2), the voltage V_i at which discharges start is given approximately by (Ref. 6):

$$V_i = E_i (t + \epsilon t') / \epsilon \quad (1)$$

where E_b refers to the gas-filled gap of thickness t' , and ϵ is the permittivity of the dielectric of thickness t . Breakdown will occur at some $V > V_i$; it is therefore essential to maximize V_i . For V_i to be high, ϵ of the medium surrounding the cavity must be low, and the cavity depth t' must be as small as possible. These discharge phenomena produce deleterious effects on plastic insulation.

Because plastics have high volume and surface resistivities, discharges which occur between opposing plastic surfaces have characteristics very different from those for discharges between metallic surfaces. The discharge current between metal electrodes flows as long as the voltage between the electrodes is maintained. For plastics, the charge which reaches the non-conducting surfaces via a discharge exerts a field in opposition to the applied field. Here, therefore, the discharge can pass only the scale current necessary to maintain the discharge. In addition, since charge transfer across the gap separating the surfaces occurs in 10^{-7} sec., only small areas can be discharged instantaneously, since the surface resistivity opposing the charge flow is high. Because of the build-up of charges on the cavity surfaces there is a distinct difference in the

discharge sequence under direct and alternating voltage. While surface resistivity remains high, successive discharge with d.c. are infrequent; but with a.c. discharges occur in each half cycle owing to the occurrence of "back discharges" when the polarity reverses.

4.2 Breakdown in "Flaws" in Foams

For our purpose we consider a foam to consist of an array of gas-filled cavities. If breakdown in solids can be controlled by discharges in the relatively few ever present cavities, then in a foam with an overabundance of cavities the same mechanism must be a virtual certainty. Since for a foam, in general, $t'/t \ll 1$, Eqn. (1) becomes

$$V_i/t \approx E_i = E_{t'}/\epsilon \quad (2)$$

Since ϵ for a foam is always smaller than that for a solid, this equation implies for a foam a somewhat higher E_i for a given cavity size. This factor which involves an average property, ϵ , affects the total foam in the same way. The breakdown strength of the gas entrapped in the cell, $E_{t'}$, depends on the nature of the gas, the pressure, and on the size and geometry of the cell. In general $E_{t'}$ increases with decreasing t' (see Fig. 4-1), and hence the fluctuation in $E_{t'}$ for cavities within a volume element will be determined by the fluctuation in cell size. This means that when the electric stress is increased gradually, discharges will initiate preferentially in larger foam cavities, with a concurrent degradation of the walls of these cavities. The eventual failure of a wall will lead to the formation of a larger cavity and hence a further decrease in E_i .

The continuation of this process will lead rapidly to further increase in the size of the cavity, and ultimately failure of the foam will ensue. In

summary, it is the size of the cavity, i.e., cell, that will determine the breakdown strength of a foam. Discharge initiation will be favored in the relatively few larger than average cells. We refer to such cells as flaws in a foam (Fig. 4-3).

The correlation between the difference in breakdown strength and the anisotropy of foam structure provided the first striking demonstration of the importance of cell size. Microscopic examination showed that in general cells are elongated in the direction of cell rise (Table 4.33-2 and -3). Thus when the foam is tested parallel to the direction of rise the applied electric field sees cell gaps which are greater than those in the perpendicular direction. For example, E_b versus density plots for the DL series of fluorocarbon blown foams (Fig. 4-4) yield two distinct curves. The higher strength corresponding to the perpendicular direction, i.e., smaller cell gap. Both curves level off for densities exceeding about 4 lb/ft³.

However, when the E_b values are plotted versus cell size a good correlation is obtained (Fig. 4-5). Incidentally, the straight line extrapolates to a value of about 200 KV/in for zero cell size, a reasonable value for the bulk polymer. For drawing of the straight line less weight was given to the low points, (i.e., left from the line), because in most cases these correspond to irregular microscopic structures. An additional demonstration of the trend for a proportionality relationship between E_b and cell size is given in Fig. 4-6. Here, the E_b and the cell length ratio correspond to the two directions of a given foam; the straight line was drawn with unit slope. One should add that Eq. 4.2-1 applies strictly to the idealized geometry shown in Fig. 4-2, whereas the geometry of foam cells

is more complicated. Therefore, no theoretical interpretation can be given at present to the above correlations, although the general trends are clearly indicated.

If the breakdown strength, E_b , were function of only the average cell size in the direction of test, then E_b should be independent of thickness. This is not the case, as shown in Fig. 3-4. The observed slopes are not unity but are about $1/2$. It is reasonable, therefore, to assume that breakdown will depend on the presence of "flaws" in the sense defined above, e.g., multiconnected cells. The distribution of such "flaws" should follow extreme value statistics, and hence, the strength should decrease with increasing volume, i.e., thickness of the test specimen. A discussion based on extreme value statistics was presented by Epstein and Brooks in their study of the breakdown of capacitours (Ref. 7).

4.3 Dependence on Rate of Voltage Application

In considering foams for encapsulant applications, it is the prediction of long-time behavior which is of interest. Endurance tests at a constant voltage simulating operatin conditions are impractical for the purpose of screening materials, becuae they are inherently time consuming. Moreover, a statistical analysis based on relatively few test results is difficult because of the following peculiarities common to this type of test: Occasionally, specimens fail while the voltage is being brought to the test value, whereas others may last several orders of magnitude longer than the mean lifetime.

The failure envelope shown in Fig. 4-7 illustrates this problem. The width of the band is a measure of the dispersion of the expected lifetime for a given voltage. Below the discharge inception voltage, V_i , no failure

will occur. For $V \gg V_i$, the expected lifetime falls within a relatively narrow time interval. But for V only slightly larger than V_i , the time interval during which failure may occur is large, and therefore, it is impossible to obtain reasonable estimates of the mean and variance from a few tests.

The situation is much brighter for tests carried out by applying the voltage at constant rate. Here, the failure envelope band is approached at a sharper angle (Fig. 4-7) and failure will in general occur within a short time interval. Fortunately, it turns out that the rate dependency of failure time is directly related to the failure time at constant voltage. In the development of the appropriate relationships, we follow the approach previously discussed in a study of electrical insulators (Ref. 8). It is of interest to point out that the problem is analagous to that of the interrelation between mechanical failure in creep and tensile failure at constant strain rate.

The basic assumption underlying the following development is that the extent of damage imparted to a dielectric during a time interval is only a function of voltage V , which is in excess of the discharge inception voltage, V_i . In addition, the total damage necessary to result in failure is a constant K , for a given material. These physical conditions can be expressed as

$$\int_0^{\tau} 1(V - V_i) f(V - V_i) d\xi = K \quad (3)$$

where τ is failure time. The unit step function is:

$$1(V - V_i) = \begin{cases} 0 & \text{for } V < V_i \\ 1 & \text{for } V \geq V_i \end{cases}$$

For any time $t < \tau$, the extent of damage D , is given by:

$$\int_0^t l(V - V_i)f(V - V_i)d\xi = kD \quad (4)$$

Clearly for $V < V_i$ no damage will occur. For constant voltage, $f(V_c - V_i)$ is a constant and Eq. (3) becomes:

$$l(V_c - V_i)f(V_c - V_i)\tau_c = k \quad (5)$$

where τ_c is the failure time at constant voltage. For solid insulators or dielectric specimens with flaws or manufactured voids, several investigators have found the following relation to hold for test results at constant voltage (Refs. 9):

$$(V_c - V_i)^n \tau_c = k \quad (6)$$

It follows from the initial assumptions that the same functional form should hold for variable voltage. For voltage applied at a constant rate λ , the voltage V , will be given by:

$$V = \lambda t \quad (7)$$

Hence, substituting Eq. (4) we have:

$$\int_0^t l(\lambda\xi - V_i)(\lambda\xi - V_i)^n d\xi = kD \quad (8)$$

Carrying out the integration between 0 and the failure time for rate λ , τ_λ , the result is

$$k = \frac{1}{\lambda(n+1)} (\lambda\tau_\lambda - V_i)^{n+1} \quad (9)$$

Thus, from test results at several rates λ , one can determine k and the

exponent n . If the initial assumptions are correct, then the same parameters are applicable for constant voltage; and hence, the life-time of the dielectric can be predicted for any condition. It is of interest to note that an equation similar to Eq. (6) was derived by applying extreme value statistics to the problem of dielectric breakdown.

Figure 3-3 shows a plot of $\log (V_b - V_i)$ versus $\log \lambda$ for the 2 lb/ft³ foam where λ is the rate of voltage application. The value 10 kv used for this plot is that for V_i in CO₂ at atmospheric pressure and a 1-in. gap. This should be the lower limit to V_i , in view of the small dimension of the cell in a foam. The upper limit must be below 19 kv, the lowest breakdown voltage observed for the slow rates. The plot in Fig. 3-3 along with Eq. (9) yields $n = 9$ and $k = 3.2 \times 10^6$. Using these values for the parameters along with Eq. (6), we estimate a failure time at constant voltage of about 5 days for $V - V_i = 2$, and about 2,000 days for $V - V_i = 1$. These calculations demonstrate dramatically the necessity of determining V_i accurately in order to make reasonable estimates of failure time. It is planned to determine V_i by direct measurements as well as by detailed analysis of more extensive studies of the rate dependence of breakdown. It should be added that the interrelation between constant and variable voltage tests may break down for materials in which significant chemical degradation is induced by means of corona. The latter would be more significant in constant voltage long-time tests.

5. Conclusions and Perspectives

The following summarizes in order of their importance the parameters

which determine the dielectric strength of a foam.

(1) Homogeneity of structure. Properties of a given foam can be optimized only if the cells are uniform in size and the content of voids or multiconnected cells is kept at a minimum.

(2) Cell geometry. Highly symmetrical cells will minimize the anisotropy of properties. Small cell size will improve strength.

(3) Gas content and type. Reducing gas pressure decreases strength. Fluorocarbons lead to much higher strength than CO_2 .

(4) Polymer distribution in the cell. It is advantageous to increase the window thickness at the expense of struts. Also, conditions during foaming should minimize stressing of windows.

(5) Density. The optimum density is 6 to 10 lb/ft^3 . In this range the foam has adequate mechanical strengths, and optimization of all the above parameters is easier to achieve. It is difficult to manufacture homogeneous higher density foams free of voids.

To complete the study discussed in this paper we are starting determinations of porosity of cells, cell volume, and thickness and size of windows. These should provide a basis for improved correlations with dielectric strength. More studies are needed on the importance of the composition and pressure. Limited experiments indicated that contamination of Freon II with small amounts of CO_2 drastically decreases strength. It is to be expected that the polymer properties should be of considerable importance in determining the resistance to degradation by discharges. Moreover, the polymer should determine to a large extent the stability of the foam toward high vacuum, U.V., heat, and its resistance to mechanical damage.

Finally we must remember that the motivation for this work was to

look at corona and breakdown at low pressures. But early studies in vacuum showed that the existing knowledge of the electrical properties of foams was insufficient to permit separation of effects of low gas pressure from other causes for failure. Now that as a result of this study the controlling influence of the cell structural parameters on breakdown has been established, some simple considerations can be used to set a lower limit to the discharge inception voltage, V_i . Paschen's Law (Fig. 1) gives about 320 volts as the potential which will initiate discharges under the most unfavorable conditions. Then for a foam the corresponding voltage should be at least 320 times the number of cells. Thus for a foam having 1 mm cells the minimum dielectric strengths should be about 8 KV/in. Olyphant and Meyer (Ref. 11) noted such an effect in a study of a type of syntactic foams (Scotchcast). Although these foams were highly porous they observed a strength of 10 KV/in. at 1 mm Hg. Their results are difficult to interpret more precisely since neither the gas pressure inside the foam nor the porosity were determined. Even so these results are encouraging. For closed cell structures higher values should be expected, for at low pressures the mean free path of a gas molecule cannot exceed the length of the cell. Our results on out-gassed urethane foams (Fig. 3-17) are consistent with this viewpoint.

Table 1. Dielectric Strength of Flexible Urethane Foam⁽¹⁾

No. of Cells Per Inch	10	20	30	45	60	80	100
E_b KV/in	36.5 ±1.2	33.3 ±0.0	35.4 ±1.2	32.8 ±1.2	32.3 ±1.2	30.5 ±0.5	34.7 ±1.0
Thickness, in	0.41	0.45	0.44	0.51	0.46	0.50	0.45

(1) Scott Paper Company; foam density 2 lb/ft³

(2) Average of five tests

Table 2. Formulations and Properties of Fluorocarbon Blown Urethane Foams

Formulation, pbw.	3079-10	3079-13	3079-17	3079-18	3079-32	3079-33	3079-34	3079-48	3079-30
Polyol A ⁽¹⁾	83.4	83.4	56.0	56.0	55.0	55.0	55.0	78.0	
Polyol B ⁽²⁾									
Polyol C ⁽³⁾									
Polyol A-TDI Prepolymer	100.0	100.0	100.0	100.0	83.0	83.0	83.0	100.0	
PAPI								31.0	
Freon R-11	28.0	40.0	22.0	28.0	27.0	21.0	33.0	1.1	
Silicone Oil SF-1079	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.6	
Silicone Oil DC-201								13.2	
Triethylenediamine	0.15	0.15	0.2	0.2	0.08	0.08	0.08		
TEACAT DME ⁽⁴⁾	1.2	1.2	1.2	1.2	1.2	1.2	1.2		
Dibutyltin dilaurate									
Phosgard C-22R ⁽⁵⁾		31.0	31.0	31.0	30.0	30.0	30.0		
Fyrol 6 ⁽⁶⁾									
Viol 82 ⁽⁷⁾									
PROPERTIES									
Bulk density lbs/ft ³	1.95	1.68	1.94	1.84	1.95	2.51	1.63	2.11	
E _b , kV/in. (unknown orientation)	72.0 ± 10	63.6 ± 10	72.2 ± 6	88.0 ± 18	80.5 ± 6	84.0 ± 8	85.4 ± 12	93.9 ± 15	84.7 ± 5
Thickness, in.	0.45 ± 0.2	0.47 ± 0.15	0.46 ± 0.10	0.30 ± 0.10	0.46 ± 0.10	0.30 ± 0.68	0.48 ± 0.10	0.32 ± 0.01	0.46 ± 0.08
No. of tests	10	9	10	10	8	10	10	5	10
E _b , kV/in. (1 to foam rise)									
Thickness, in.									
No. of tests									
E _b , kV/in. (11 to foam rise)								109.4	
Thickness, in.								0.265	
No. of tests								1	

(1) Propylene oxide adduct of sorbitol; mol. wt. 700.

(2) Propoxylated Mannich reaction product from phenol-diethanolamine-formaldehyde (molar ratio 1:3:3); equiv. wt. 350.

(3) Same as 2, but equiv. wt. 650.

(4) Jefferson Chemical Company.

(5) Monsanto Chemical Company.

(6) Victor Chemical Division, Stauffer Chemical Company.

(7) Mobil Chemical Company

Table 2. (Continued)

Formulation, pbw.	3111-2	3111-3	3111-4	3111-5	3057-36-2	3024-17-35	3024-28-4
Polyol A ⁽¹⁾	65.0	78.0	65.0	78.0	17.15	36.6	33.4
Polyol B ⁽²⁾					17.15		
Polyol C ⁽³⁾					47.1	47.9	48.7
Polyol A-TDI Prepolymer							
PAPI	99.0	100.0	99.0	100.0			
Freon R-11	28.0	33.0	28.0	36.0	13.0	15.0	12.5
Silicone Oil SP-1079	1.0	1.2	1.0	1.1			
Silicone Oil DC-201					0.6	0.5	0.5
Triethylenediamine	0.6	1.0	0.8	0.4			
TEACAT DME ⁽⁴⁾							
Dibutyltin dilaurate						0.03	0.006
Phosgard C-22R ⁽⁵⁾		30.0					
Fyrol 6 ⁽⁶⁾	13.0		13.0		5.0		4.9
Vircol 82 ⁽⁷⁾							
PROPERTIES							
Density lbs/ft ³	2.08	2.18	2.03	1.72	1.95	1.75	2.08
E _b unknown orientation	96.0 ±14	98.8 ±12	93.9 ±19	106.4 ±9	158.6 ±13	144.1 ±17	133.6 ±29
Thickness, in.	0.35 ±0.02	0.35 ±0.02	0.26 ±0.06	0.32 ±0.02	0.25 ±0.02	0.18 ±0.08	0.24 ±0.04
No. of tests	5	4	6	7	6	9	9
E _b , kV/in. (11 to foam rise)					153.5 ±10	152.8 ±2	146.7 ±2
Thickness, in.					0.26 ±0.01	0.24 ±0.01	0.26 ±0.01
No. of tests					3	2	2
E _b , kV/in. (11 to foam rise)					106.9 ±10	147.2 ±2	98.8 ±1
Thickness, in.					0.25 ±0.02	0.26 ±0.01	0.26 ±0.00
No. of tests					3	2	2

Table 3. Effect of varying density and cell size on properties of Formulation 3111-5 from Table 2.

Code DL	Density lbs/ft ³	Fill content		Measurement direction								Strut thickness mm	Length ratio (paral. / perpend.)	E _b ratio (perpend. / paral.)
				Parallel to rise				Perpendicular to rise						
		pbw	%	Cell length mm	Thickness in.	E _b kv/in.	Cell length mm	Thickness in.	E _b kv/in.					
1	2.14	37	16.2	1.60	0.25 ±0.04	82.8 ±7.3	1.20	0.23 ±0.03	123.1 ±11.0	0.11 ±0.01	1.33	1.48		
2	2.28	30	14.4		0.25 ±0.01	90.2 ±24.0		0.25 ±0.01	123.7 ±13					
3	3.0	25	12.2	1.28	0.25 ±0.02	106.6 ±10.0	0.96	0.24 ±0.01	140.5 ±15	0.07 ±0.01	1.33	1.37		
4	3.43	20	10.0	1.26	0.25 ±0.01	116.3 ±6.0	0.90	0.24 ±0.01	135.1 ±18.0	0.07 ±0.01	1.40	1.17		
5	4.72	15	7.7	1.09	0.26 ±0.02	126.3 ±5.0	0.90	0.24 ±0.005	140.2 ±8	0.050 ±0.01	1.21	1.11		
6	8.19	10	5.3	0.70	0.26 ±0.02	131.1 ±11.0	0.62	0.24 ±0.004	141.4 ±0.242	0.09 ±0.01	1.13	1.08		
7	15.4	5	2.7	0.56	0.26 ±0.03	121.3	0.36			0.09 ±0.01	1.56			
8		0	0											

Table 4. Effect of varying density and cell size on properties of Formulation 3024-17-35 from Table 2.

Code IE	Density lbs/ft ³	Fill content		Measurement direction						Strut thickness mm	Length ratio (paral. / perpend.)	Eb ratio (perpend. / paral.)
				Parallel to rise			Perpendicular to rise					
		pbw	%	Cell length mm	Thickness in.	Eb kv/in.	Cell length mm	Thickness in.	Eb kv/in.			
1	2.29	15.0	14.9	0.96	0.233 ±0.005	104.9 ±12.0	0.70	0.236 ±0.008	153.6 ±5.5	0.035 ±0.01	1.37	1.57
2	2.52	13.0	13.3	1.16	0.221 ±0.004	97.3 ±17.0	0.72	0.237 ±0.003	156.4 ±5.2	0.05 ±0.01	1.55	1.56
3	2.57	11.0	11.5	0.92	0.259 ±0.015	104.4 ±11.0	0.74	0.244 ±0.008	153.1 ±3.6	0.04 ±0.01	1.24	1.47
4	3.48	9.0	9.6	0.87	0.249 ±0.010	94.5 ±32	0.48	Poor quality		0.035 ±0.01	1.85	
5	12.0	7.0	7.7		0.272 ±0.011	53.7 ±9.7				0.07 ±0.01		
6												
7	3.28	10.0	10.6	0.78	0.243 ±0.004	100.2 ±15.2	0.60	0.246 ±0.012	139.9 ±16.0	0.07 ±0.01	1.30	1.39
8	8.0	8.0	8.7		0.248 ±0.011	83.3 ±8.3		Very poor sample			0.065 ±0.01	
9	1.67			1.6	0.234 ±0.01	67.1 ±22	1.03	0.254 ±0.01	106.2 ±41	0.06 ±0.01	1.55	1.34
10	1.84			2.15	0.251 ±0.02	63.5 ±14.0	1.20	0.265 ±0.02	147.5 ±16	0.04 ±0.01	1.80	2.33
11	1.45	26.2	23.6	0.92	0.232 ±0.02	61.8 ±3.0	0.73	0.228 ±0.02	130.9 ±13.1		1.26	2.11

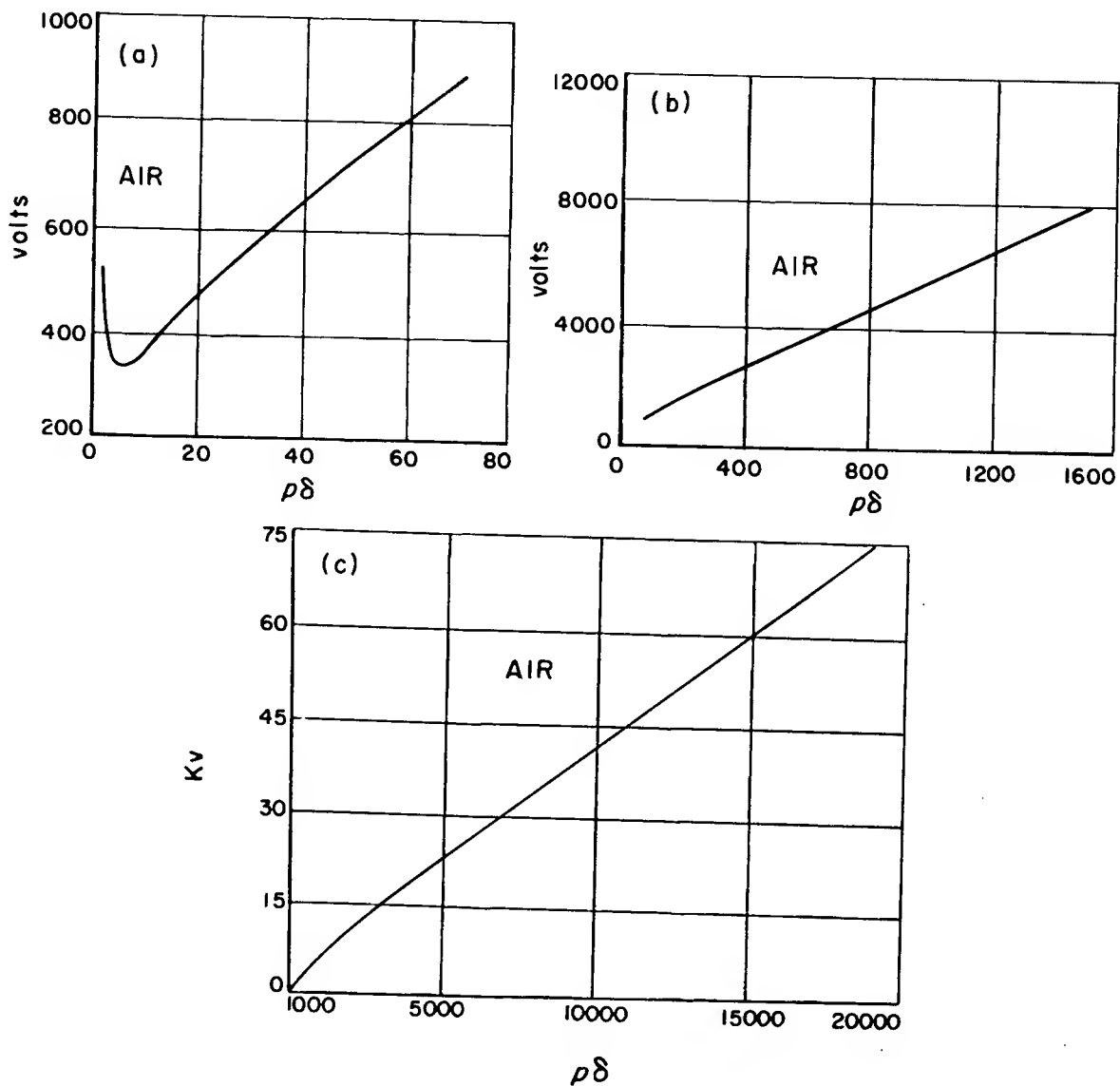


Fig. 1-1 Arcing voltage versus product of pressure and separation of parallel plate (Paschen's Law)



Fig. 2-1 Dielectric Strength Test Set, Model PDA-1 (Industrial Instruments Inc.)

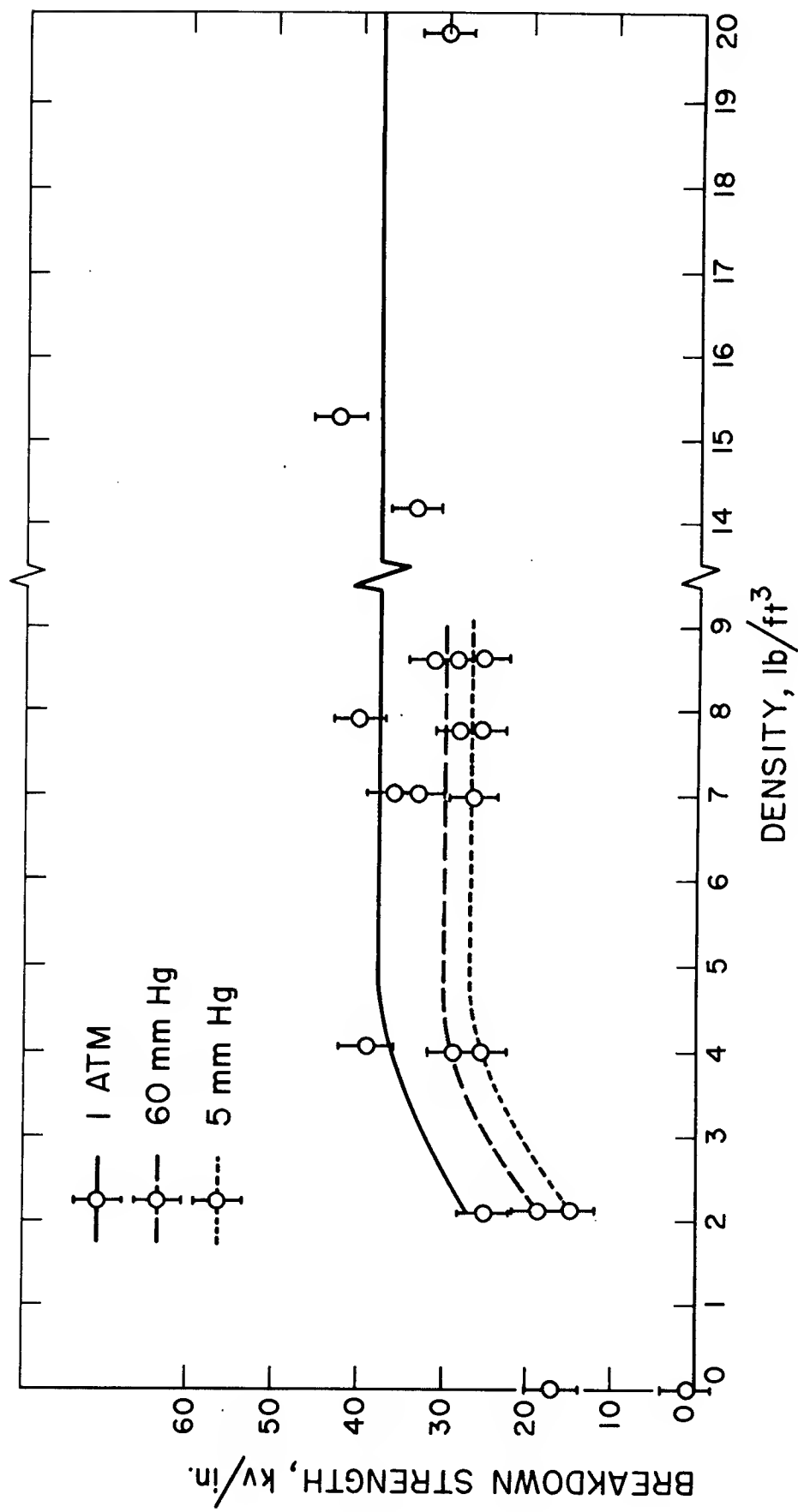


Fig. 3-1 Breakdown strength versus density for Eccofoam

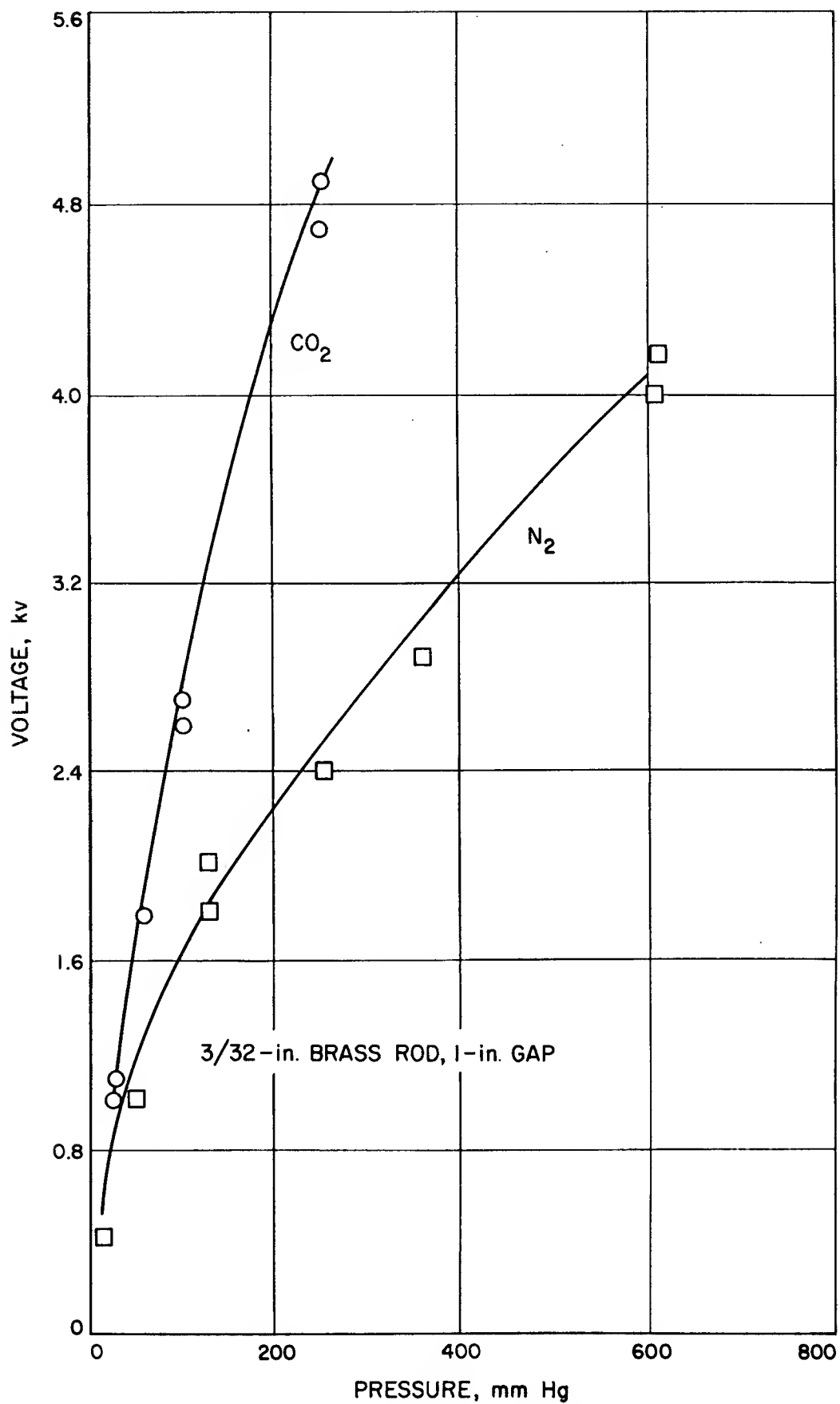


Fig. 3-2 Voltage at onset of corona or pressure for CO₂ and N₂

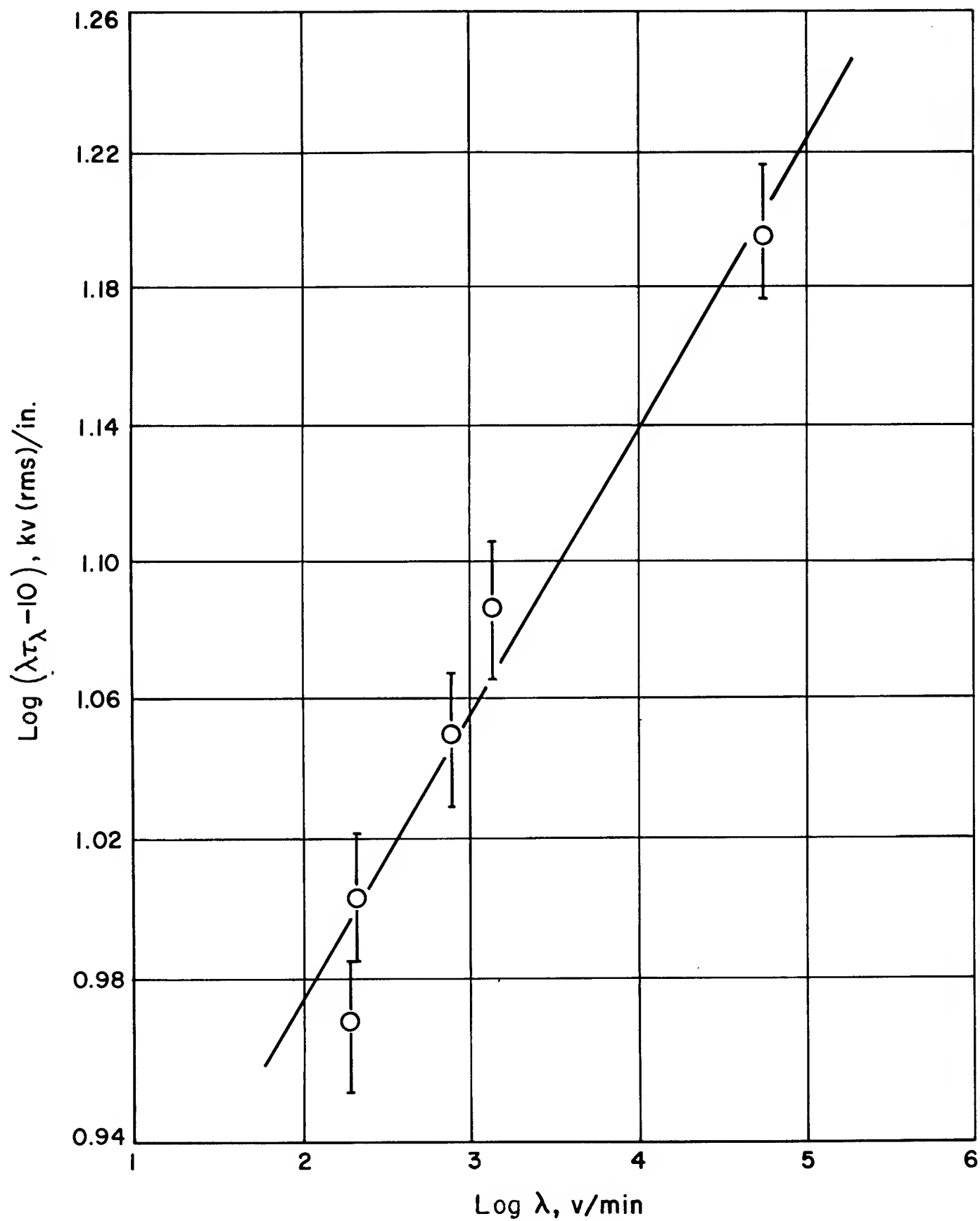


Fig. 3-3 Dependence of breakdown voltage on rate (Eccofoam, 2 lb/ft³)

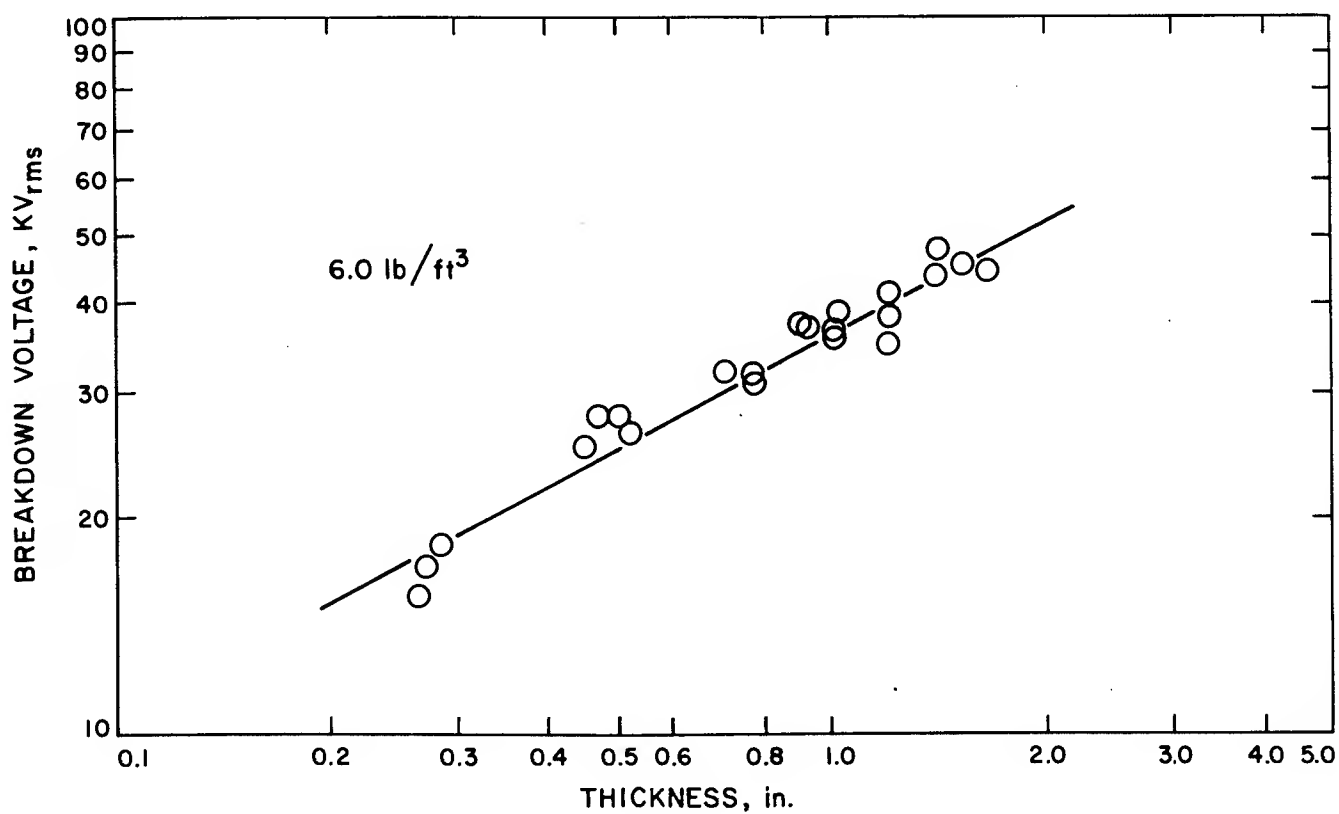
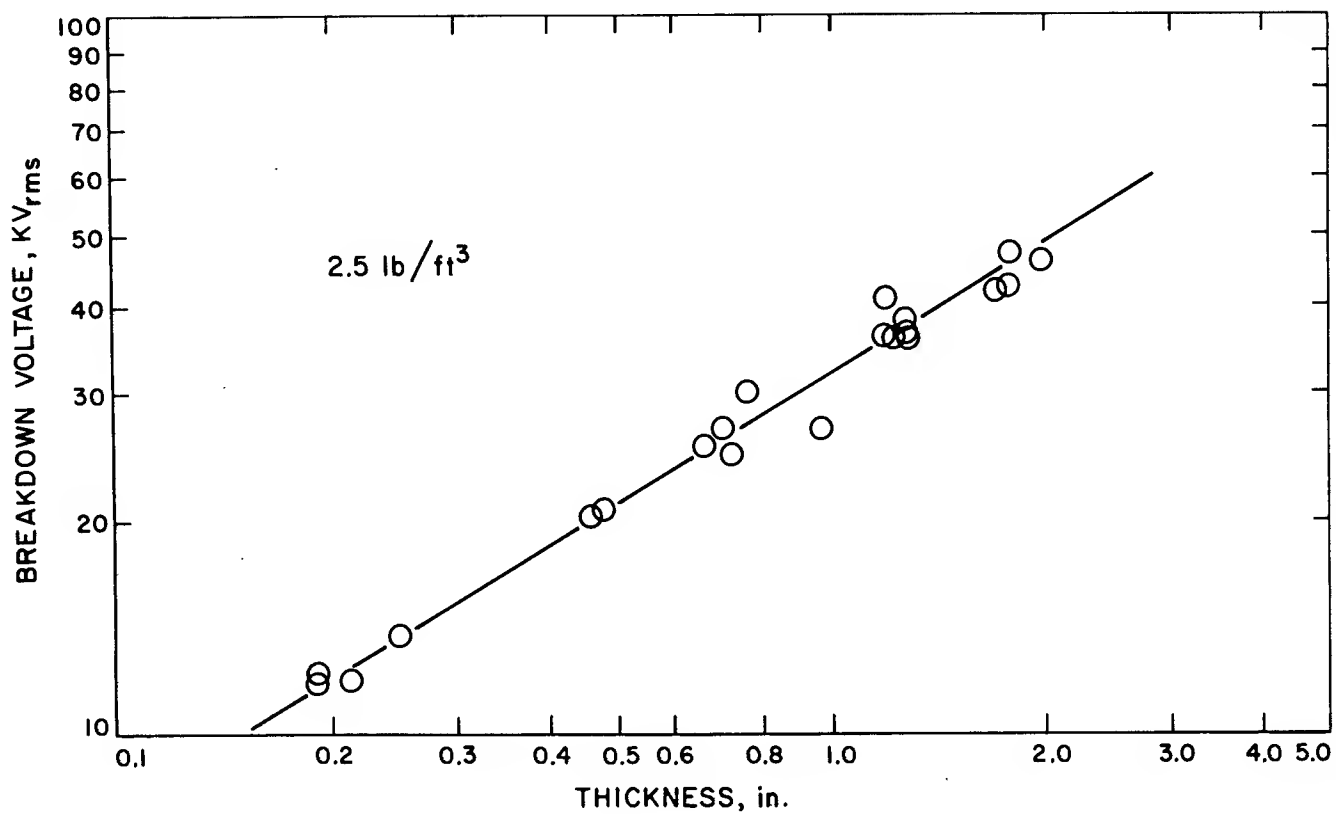


Fig. 3-4 Dependence of breakdown voltage on sample thickness (Eccofoam)



DL-3



DL-6



IE-10



IE-7

Fig. 3-5 Examples of cell structure (magnification 80 x); DL-3 and IE-10 fall on the line in Fig. 4-5, DL-6 and IE-7 have flaws and fall below the line

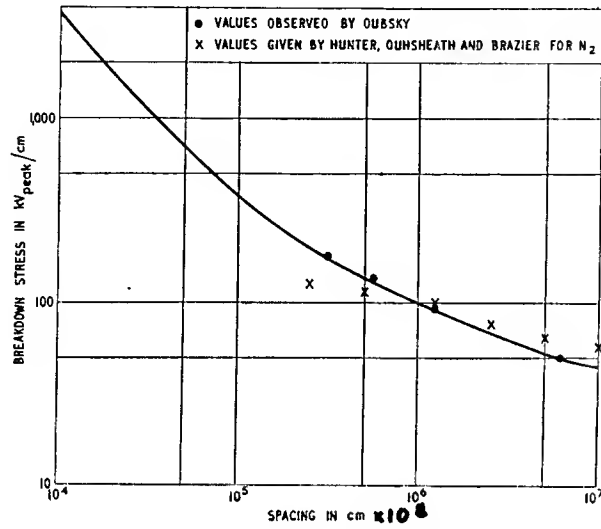


Fig. 4-1 Variation of breakdown strength with spacing for air at 20°C and 76 cm Hg

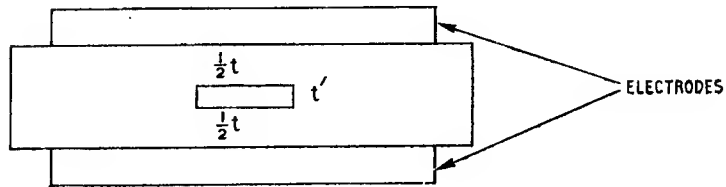


Fig. 4-2 An idealized void in a solid

VOID IN SOLID DIELECTRIC

"VOID" IN CLOSED-CELL FOAM

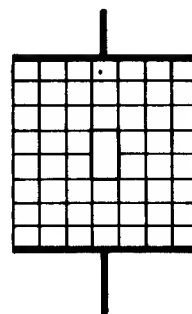
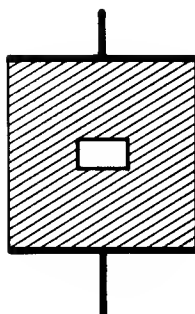


Fig. 4-3 A void or flaw in a foam

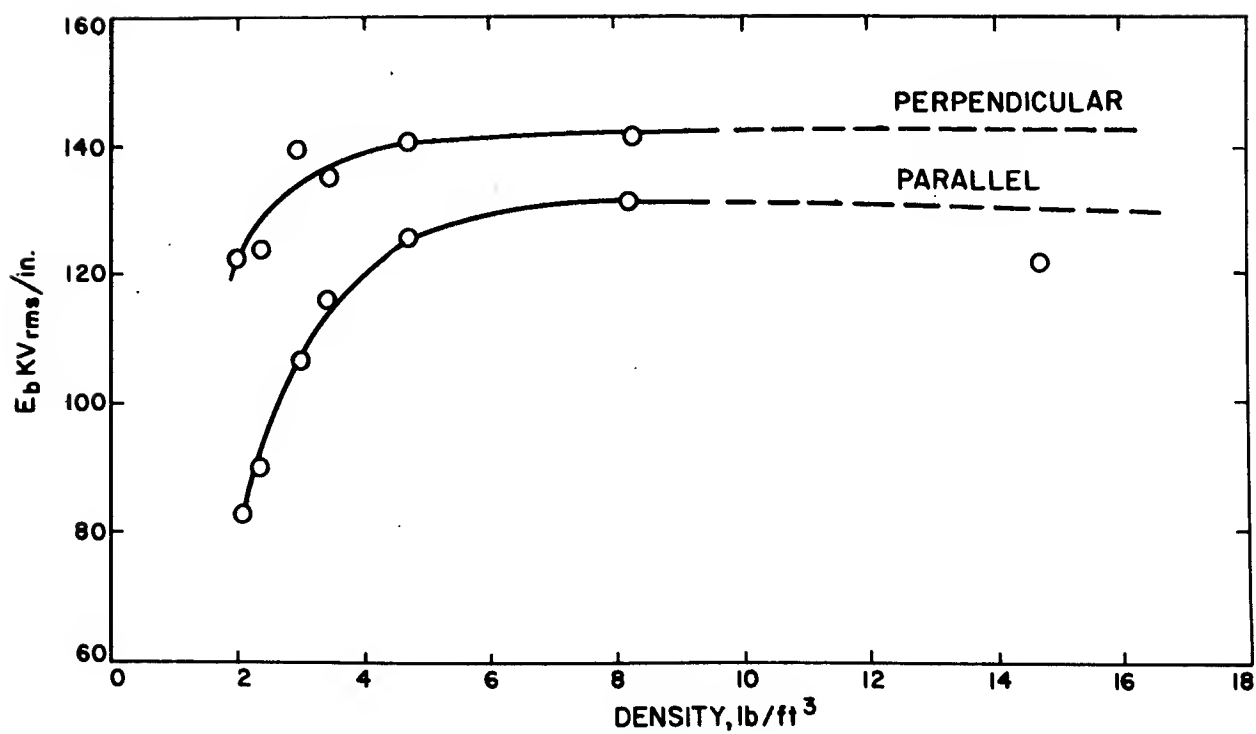


Fig. 4-4 Difference in dielectric strength with direction of foam rise

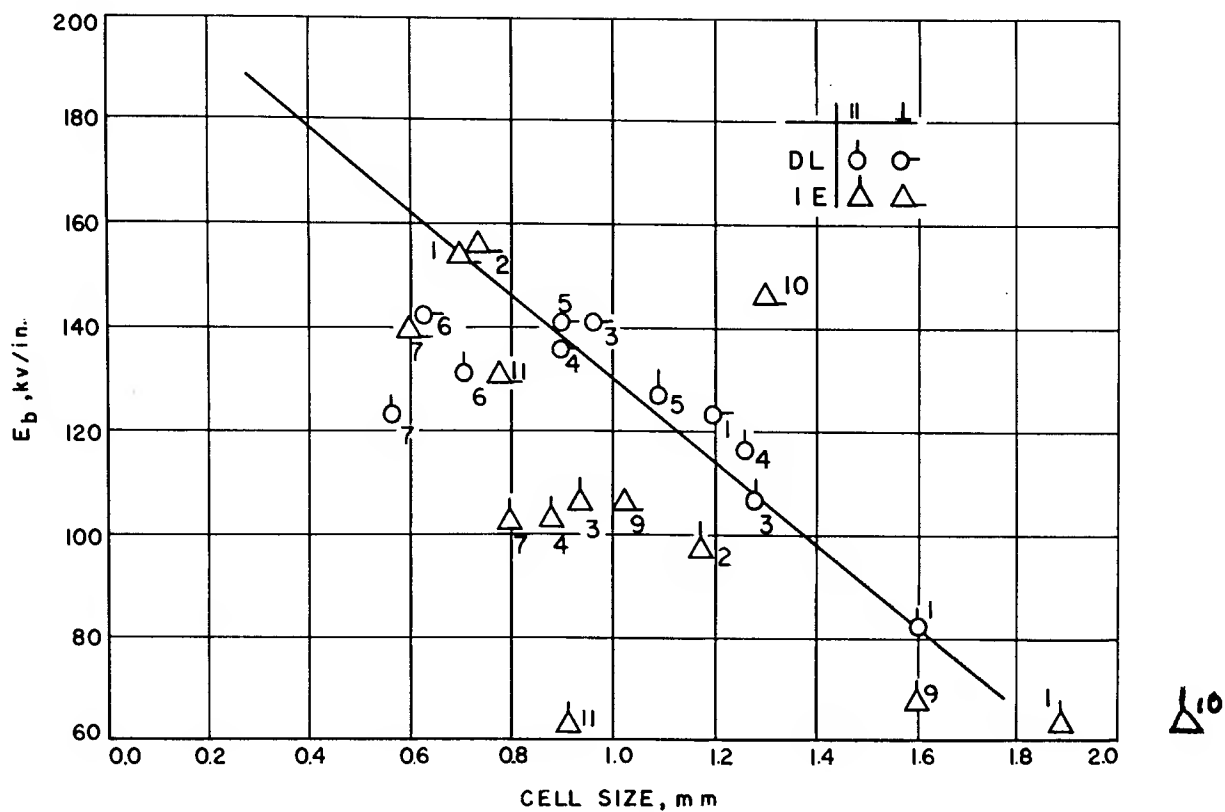


Fig. 4-5 Variation of dielectric strength with cell size

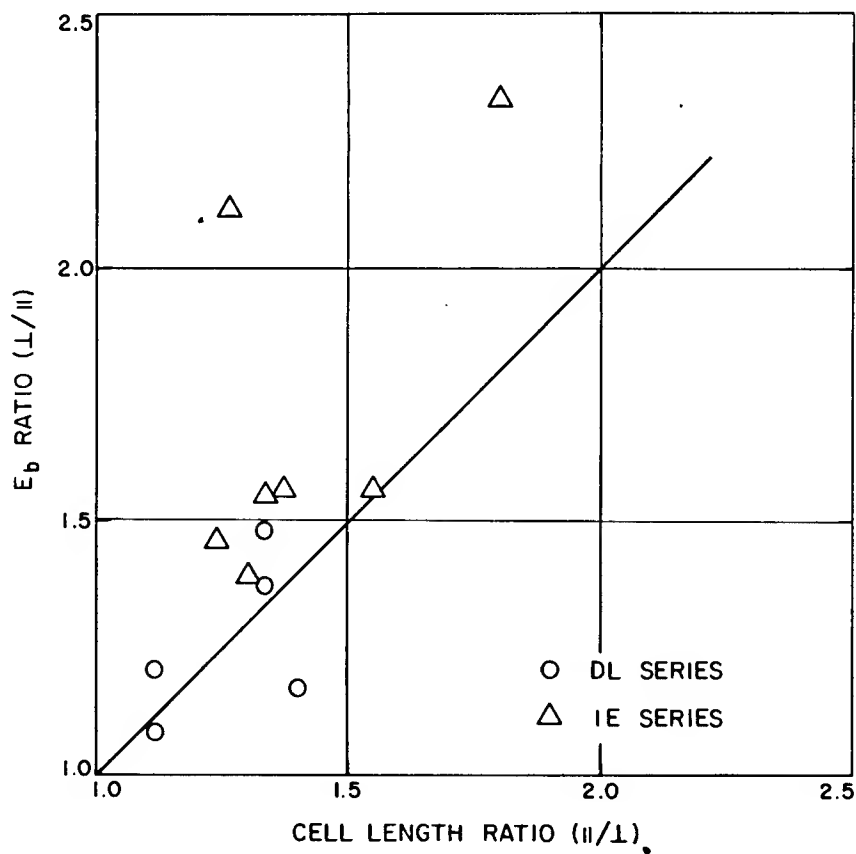


Fig. 4-6 Correlation between dielectric strength and cell size anisotropy

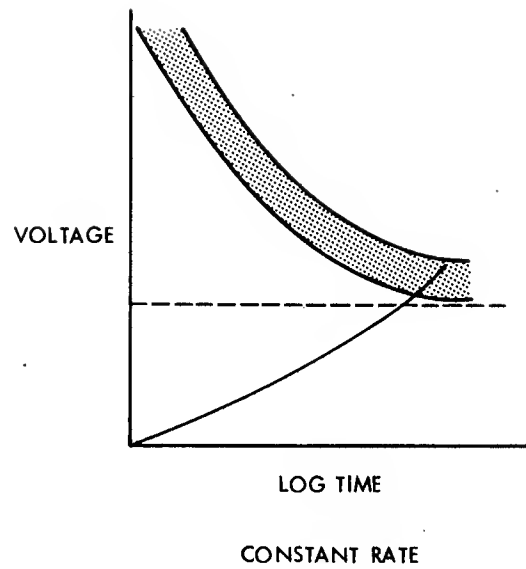
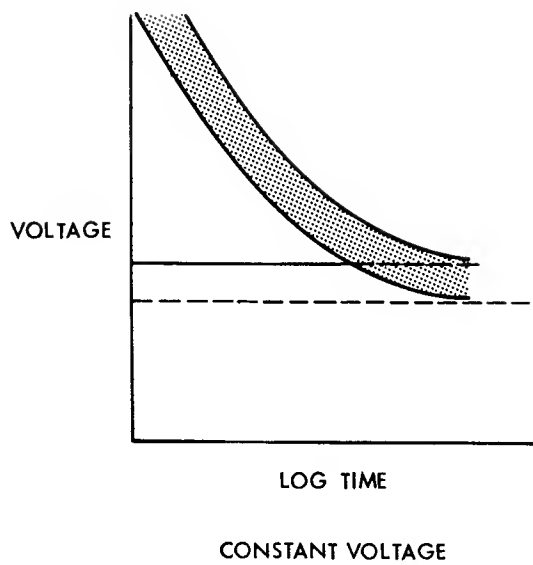


Fig. 4-7 Hypothetical dielectric failure envelopes

References

1. E. R. Bunker, Jr., in Proceedings of the Workshop on Voltage Break-down in Electronic Equipment at Low Air Pressures, E. R. Bunker, Jr., Editor, Jet Propulsion Laboratory Technical Memorandum 33-280, Pasadena, California, 1966, 321.
2. K. Woo, Jet Propulsion Laboratory Space Programs Summary 37-44, Vol. IV, Pasadena, California, May 1967.
3. R. Boundy, Ref. 1, pp. 33.
4. a. E. F. Cuddihy and J. Moacanin, Journal of Cellular Plastics, Vol. 3, No. 2, 73 (1967).
b. F. J. Norton, *ibid.*, Vol. 3, No. 2, 23 (1967).
5. K. N. Mathes, "Electrical Properties," in Engineering Design for Plastics, E. Baer, Editor, Reinhold Pub. Co., 1964, pp. 441-588.
6. N. Parkman, "The Electrical Properties of High Polymers," in Physics of Plastics, P. D. Ritchie, Editor, P. Van Nostrand Co. Inc., 1965, pp. 285-322.
7. a. B. Epstein, Journal of Applied Physics, 19, 140 (1948).
b. B. Epstein and H. Brooks, *ibid.*, 19, 544 (1948).
8. W. Starr and H. Endicott, AIEE Trans. Pwr. App. and Syst., Vol. 80, Pt. III, 515 (1961).
9. G. L. Moses, AIEE Trans., Vol. 70, Pt. 1, 763-769 (1951).
10. V. M. Montsinger, *ibid.*, Vol. 54, 1300-1301 (1935).
11. M. Olyphant, Jr. and C. L. Meyer, "Light Weight and Corona Suppressant Encapsulants for Aerospace Industries," paper presented at NEPCON Convention, Long Beach, California, June 1965.

Wayne State Univ.
Polymer Conf.
May 1967

10214-8

TESTING OF CELLULAR PLASTICS

By

William A. Ashe

Wayne State Univ.

The testing of cellular plastics has been the subject of concern to a number of agencies, the least of which has not been the American Society for Testing and Materials. Under the standardization procedure of ASTM, responsibility for flexible foam specifications and testing procedures have been placed under the jurisdiction of Committee D-11 on Rubber and Rubber-like Materials and specifically under Subcommittee 22 on Flexible Cellular Materials. Rigid foams have been assigned to Committee D-20 on Plastics, Sub 22 on Rigid Cellular Plastics.

Over the years Sub 22 of D-11 has developed several methods and standards. These include D-1055 for latex foam, D-1056 for sponge and expanded cellular rubber products, D-1564 for urethane foams, D-1565 for flexible foams made from polymers and copolymers of vinyl chloride, D-1667 for sponges made from closed cell poly(vinyl chloride) or copolymers thereof, and, the most recent, D-2406 for molded urethanes. For the most part these documents are complete and they contain subsections devoted to all the usual properties such as density, compression set, heat aging and compression load.

For rigid foam each test is usually devoted to one particular property, in the appendix you will find a complete list of the ASTM designations used for cellular materials.

Other organizations and code agencies have also issued methods and specifications. These include the automotive companies, building and coding groups, federal and state governments and lastly the International Organization for Standardization (ISO).

The ISO has two groups working on cellular products, ISO/TC 45 on flexibles and ISO/TC 61 on rigids. It is the hope of this international group to have all flexible foams tested according to one test method. Concerning rigid foams, most of the U. S. methods have been accepted as the basis for the ISO document and are already being used by the common market countries. For the purpose of this discussion we will divide the paper into two parts. Part I on flexible foams and Part II on Rigid Foams.

PART I

FLEXIBLE CELLULAR PASTICS

INTRODUCTION

It would be nice to start out by giving an approved definition for the term "flexible foam", but this is not possible simply because there is none. We can characterize them by saying they do not have a yield point when compressed, they do have high resilience and recovery when deformed, and when a specimen 8"by 1"by 1" is wrapped 180 degrees around a 1 inch mandrel at moderate speed they do not rupture or break.

DENSITY

Density is the one property that underlies all properties of expanded materials. All properties such as strength, tear, resilience, etc. are predicated on density. Density is weight per unit volume of foam. It is determined by direct measurement and computation.

The length, width and thickness are measured to the nearest practical unit. Small samples are measured to the nearest 0.001 inch, while larger samples to within 1% of the dimension. The weight is determined to the nearest 1%. The density can be calculated as:

$$D = \frac{W}{V}$$

where D is the density in pounds per cubic foot,

W is the weight in pounds, and

V is the volume in cubic inches.

If the weight is in grams, the factor, 3.81, is used to convert all units to pounds per cubic foot.

$$D = \frac{W}{V} \times 3.81.$$

Sectional density is determined on a section of foam usually having a minimum dimension of 15 by 15 by specimen thickness. This is also called the ILD density since the Indentation Load Deflection specimen is used for the determination. The core density is determined on a specimen free of skins and has the minimum volume of 1 cubic inch.

CELL SIZE AND SHAPE

Cell size and shape is also dependent on density. The cell shape of a high density foam tends to be spherical and low density foams elongated. Expanded plastics of about 30 pounds per cubic foot will have a round cell, while at lower density, the cells will have a tendency to become completely elongated, and egg shape. The cells per inch, or pore count, are usually independent of density. Most commercial foams, depending upon their application, will vary between 10 and 100 cells per inch. Tensile, tear, and air flow are affected by cell size. As important as

this property may be, there is no established procedure for determining cell size or cell count. Part of this dilemma arises from the desire of the researcher to measure precisely a property when the property itself may vary more than the precision of the equipment allows. While average cell size is a realistic concept, an effort has been made in Subcommittee 20 to measure this particular property. For the past several years two committees have worked on methods of determining the number of cells per inch. Most of the difficulties arise because of the anisotropy of the cells. The length of the cells versus the width of the cells, and where the measurement is to be made and what type of equipment is to be used. It is hoped that in the near future some realistic method can be used to ascertain cell size. A Symposium was held at the Annual ASTM Meeting in June of 1966 on the Resinography of Cellular Materials. Eight papers were presented which discuss in detail cell size measurements, cell configuration, cell structure (such as the struts and the cell window) and other properties related to resinography-type measurements and studies.

AIR FLOW MEASUREMENTS

The air flow test measures the ease with which air passes through

a cellular structure. The test consists of placing a flexible foam specimen into a test cavity and creating a specified constant air pressure drop across it. The rate of flow of air required to maintain the pressure drop (ΔP) is the air flow value.

Since 1960 several different types of instruments have been constructed to measure the breathability of foams. The SPI has conducted several round robins and the final method was submitted to D-11 of ASTM in February 1967 at the Detroit meeting. Jones and Fesman report that air flow values are related to cell structure and can be related to certain physical properties like ball rebound, compression load deflection and flex fatigue. Air flow is recommended as a new parameter for describing flexible foam cell structure. A similar method is already part of the ISO test procedures.(Figure 20)

RESILIENCE

The resilience of a urethane foam is determined by the ball rebound method. This is also known as the Nopco Falling Ball Test. There is no established procedure for determining the resilience of latex, vinyl and other flexible cellular products. Some of the tests used in the past have included the impact resilience

* R. E. Jones and G. Fesman, J. Cellular Plastics, Vol. 1, No. 1, Jan. 1965.

and penetration of rubber by the rebound pendulum, and the test for mechanical properties of the elastomers, vulcanizates under compression or shear strain by the mechanical oscillograph method.

The ball rebound test is one that consists of dropping a steel ball on a foam specimen and noting the height of the rebound. A steel ball 0.625 inches in diameter weighing 16.3 grams is dropped on the inside of a clear plastic tube 1-1/2 inches in diameter from a test height of 18 inches. The rebound is noted and converted to a percent rebound. Since it is most convenient to note the position of the top of the ball on rebound, the top of the ball shall be 18.625 inches above the surface of the foam. Thus the zero rebound shall be 0.625 inches or the diameter of the ball above the specimen surface. A scale on the back of the plastic tube can be calibrated directly into percent rebound. The test specimen shall have parallel top and bottom surfaces. The test specimen can consist of the entire product or a suitable portion thereof, except that in no case shall the thickness be less than 2 inches or the area less than 16 square inches. Specimens of less than 2 inches should be plied up without the use of cement to a minimum thickness of 2 inches. Three specimens are usually tested. The three specimens may

be obtained by using separate items or, when convenient, three different locations on the same item. The center of the specimen is placed at the base of the tube and the tube is adjusted so that it just barely touches the surface of the foam specimen. The steel ball is released by a magnet or some other mechanism and is dropped onto the top of the foam. The maximum height of rebound is noted. If the ball strikes the tube on the drop or on the rebound, the value obtained is invalid. The ball is dropped several times, at least three, and an average value is obtained. The rebound test is also run on molded foams. Often-times the test is run on the molded surface or on a core specimen. The type of specimen should be noted in the report.

This method is arbitrary as to the size of the ball, the height of the column and the procedure. Consequently, this type of resilience has no relationship whatsoever to the resilience measured in other types of elastomeric products. This method cannot be used to determine the hysteresis properties of cellular foams where hysteresis and resilience add up to 100%.

The effect of closed cells or the effect of trapped air in open cells is referred to as a pneumatic effect. Attempts have been made in investigating this test to run this rebound procedure

in a vacuum, but since there is no apparent relationship of this value and performance, the subject did not receive intensive research.

The highly resilient foam tested by this procedure will yield a rebound value of 50 to 60% where other foams of stiffer or boardier nature may yield values of only 25 or 30%. It is quite obvious that super-soft foams will be penetrated deeper by the ball and may exhibit less rebound, and therefore, less resilience than firmer foams. In the last year or so the magic number of 55% has been developed for filled foams. Some people believe that a 4-inch sample (note - not according to ASTM in thickness) when tested should yield at least 55% rebound or the filled foam in some way is inferior. This is the type of concept that develops when there is no clear indication that the data represented by this 55% rebound does guarantee performance in the field. Resilience is one property that is not normally listed on most specification sheets.

At the Prague Meeting of the ISO in November of 1966, it was recommended that the ball rebound method be deleted from the international standard.

The concept of resilience under load may have some value. This idea involves measuring the response of a foam to dynamic flexing under fixed limits of deflections or loads. In other words, to what degree does a person bounce up and down while riding on a rough road and what percentage of this rebound or resilience is contributed by the foam and what part by the attendant suspension elements.

TENSION TESTING

The tension testing of all flexible cellular foams is done according to ASTM D-1564 or D-2406. It is interesting to note at the beginning of the discussion, that there is no tension requirement for latex foam, sponge foam or other non-urethane products. The tension test determines the effect of the application of a tensile load to foam. Measurements are made for tensile strength, tensile stress and ultimate elongation.

The dumbbell shape specimens are prepared using the die in Figure 1. The die should be sharp and free of nicks in order to prevent leaving ragged edges on the specimen. The width of the specimen is taken as the width of the die which is 1/2 inch. The thickness is usually also 1/2 inch but for some foams used for crash pads and other applications, the specimen sample may be thinner. Since the constricted portion of the die is

1/2 by 1/2, the direction of the plane from which the specimen is cut will usually have no effect upon the results. Five specimens are prepared. The thickness of each dumbbell is measured taking care the measuring gage does not distort the foam.

The distance between the self-aligning grips is set at 2.5 inch and the rate of loading is 20 inches per minute. The tensile strength is calculated by dividing the load in pounds at rupture by the original cross-sectional area and reporting the value in pounds per square inch.

The tensile stress can be calculated at any desired strain.

The 100% stress value is most often reported.

The ultimate elongation is calculated by subtracting the original distance at rupture and expressing the difference as a percentage of the original distance.

For machines equipped with a load stop sensing device, the cross-head travel can be read from the extension dial at the moment of rupture. For machines equipped with a synchronous chart drive, elongation can be measured from the chart paper. This seems like a simple test which should be easy to run and highly reproducible between laboratories. Table I shows the results

obtained from a recent SPI round robin. The wide variation can be attributed only to the failure of laboratories to follow the prescribed procedure.

TABLE I
SPI ROUND ROBIN, MARCH, 1966
URETHANE FOAM STUDY
Foam Density 1.5 to 1.7 pcf.

<u>Company</u>	<u>Tensile, psi.</u>	<u>Elongation, %</u>
A	18.2	265
B	19.0	260
C	17.5	224
D	20.2	245
E	18.5	262
F	19.3	209
G	16.2	210
H	16.5	250

There is good agreement in the tensile determinations and very poor agreement in the measurement of elongation.

The die recommended for urethane foam does not have the same radius of the shoulder as Die "A" in ASTM D-412 which is used in some of the automotive standards. The urethane die has

particular dimensions which enables the elongation to be measured as a function of the cross-head motion, hence the elongation can be taken from the chart paper or the extension dial.

When using Die "A" bench marks are placed on the middle portion of the dumbbell 1 inch apart on center. The distance between the bench marks is measured to the nearest 1/10 of an inch and the elongation calculated in the normal method.

A comparison of the two methods shows that there may be a difference of 15 percentage points with Die A giving the lower value. Part of this difference is due to the configuration of the dumbbells and part to the minor slippage that occurs in the gripping mechanism.

When foams of less than 1/2 inch in thickness are tested this should be included in the report since they will not be equal to the results obtained on the 1/2 inch specimen.

TEAR RESISTANCE TEST

The tear resistance test is covered in detail in D-1564 for urethane foams but is not mentioned as a specific test requirement for vinyls and latex foams. In these latter two foams, the test

method and value are to be arranged between the purchaser and the manufacturer and in almost all specifications this test has not been considered pertinent enough to be included. The tear method used for urethane foams is called the block tear method. The block method produces a value which may be regarded as a measure of the tear resistance under the conditions of this particular test. The block specimen measures 6 inches long by 1 by 1 with a slit cut down the center 1-1/2 inches deep (Fig. 2). The tear resistance is usually measured on a power driven apparatus which will indicate the final load at which the rupture takes place. An automatic machine such as an Instron may be used which will draw the actual curve or an instrument like the Scott tester can be used where the maximum load can be indicated. The travel of the actuated grips shall be 2 inches per minute. The test specimens are usually cut with a scalloped blade saw from sheets or blocks of foam. The sides are parallel and perpendicular to each other, the specimen cut from molded foam should be free of stratification layers and of skin. Three specimens usually constitute the test. The value reported shall be the mean of those tested. If any value deviates more than 20% from this mean, two additional specimens shall be tested. The mean for all five values should then be reported.

The specimen is clamped into the jaws of the testing machine taking care that the jaws fit the specimen properly. Spread the blocks so that each tab is held in the jaw to pull across the specimen. The load is applied at 2 inches per minute, aid the cut in the specimen with a razor blade or a knife so that the tear is kept in the center of the block. After the rupture of the specimen or at least two inches length is torn, record the maximum reading on the dial or scale and note also the thickness of the specimen. It is common to see the tearing response as a serrated line recorded on the chart paper. Therefore, only the highest load obtained shall be used as the tear value. Some foams exhibit the effect that the longer you tear the specimen, the higher the tear value will be, but at a certain point, usually after an inch or an inch and three-quarters of tearing, the load will begin to level off and can be used as the maximum value for the test. The maximum load registered on the machine is recorded, if the thickness is less than 1 inch, the tear is calculated by dividing the thickness into the load.

Sufficient work has been done in many laboratories to indicate that this speed of testing has very little effect upon the final results, Table II.

TABLE II
TEAR STUDY

<u>Crosshead Speed</u>	<u>Sample</u>			
	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
2 "/min.	2.3	2.3	2.2	1.6
5 "/min.	2.3	2.5	2.2	1.7
10 "/min.	2.4	2.5	2.2	1.9
20 "/min.	2.2	2.6	2.3	1.8

Other test methods are sometimes specified. These include the Graves tear which is Die C (Fig. 3) and trapezoid tear which is an experimental tear method. The Graves tear is measured according to ASTM D-624-54, "The Standard Method of Test for Tear Resistance of Vulcanized Rubber." This, of course, is often referred to as the unnicked 90° angle tear test. It is interesting to note that in this tear, the sharper the die and the more precise the 90° angle, the lower the value obtained. Where when the die gets dull or the angle changes, the tear value will usually increase. Unlike the rubber test, no lubricant or water is used to facilitate dieing out the specimen. This test has been found very very beneficial for use in foams that are firm and have a tendency to have low elongations, such as

some of the filled, high density and medium density semi-rigid foams. The rate of loading is 20 inches per minute.

Another tear test which has been used considerably is the trapezoid tear (Figure 4). Some people have noted that there appears to be a relationship in solid urethanes between the trapezoid tear and the cross-linked density. Values obtained by the 1564 method, the Graves tear and the trapezoid tear are given below in Table III.

TABLE III
COMPARATIVE TEAR RESULTS

<u>Method</u>	<u>Sample A</u>	<u>B</u>	<u>C</u>
D-1564	2.0	3.7	0.9
D-624	3.4	4.8	3.0
Trapezoid	7.2	9.4	5.2

Sample C is a semi-rigid foam used in a crash pad application.

COMPRESSION SET

Compression set tests are intended to measure the ability of a foam to retain elastic properties during prolonged action of compressive stresses. For the purpose of this test, compression set of a foam shall be considered as the residual decrease in thickness of the specimen measured after a period of time from the removal of a suitable loading device in which the specimen

has been subjected for a definite time to the compressive deformation under a specific condition of temperature. There are two specified methods in ASTM: Method A, compression set under constant load and Method B, compression set under constant deflection. Compression set under constant load has been studied for flexible foams, but it is not part of any test method or specification. Method B compression under constant deflection is part of almost all flexible foam specifications and test methods. Since latex, urethanes and vinyl foams are tested in a slightly different manner, each one will be treated separately.

LATEX FOAMS - TEST SPECIMENS - Specimens shall consist of having parallel top and bottom surfaces, usually skin on only one surface. A cylinder 1.129 inches in diameter shall be suitable for both slab and uncured stock. For cured stock the specimen may be either round or rectangular. The minimum dimensions on the top and bottom surfaces must be greater than the height of the sample and the surface shall have a minimum area of 16 square inches. Thickness of the specimen may vary but should not be less than $\frac{3}{4}$ of an inch for slab or uncured stock. The thickness shall be measured and given in the final report. The specimen height is measured to the nearest 0.001 inch, placed in the compression

set jig and compressed to 50% of the original thickness, and held for 22 hours at 70°C (158°F) in an air circulating oven. The compression deflection jig can consist of any rigid material, steel, aluminum or even wood provided it does not bend or warp. Once the sample is measured and placed in the compression set deflection jig, it is usually placed within 10 minutes into the oven. After 22 hours, the test jig is immediately removed, the specimens released and placed on a non-conductive surface for 30 - 0 + 10 minutes. The thickness of the specimen is then remeasured and the compression set calculated.

The calculations can be based on either the percent of original height or percentage of deflection.

Compression Set

$$\% \text{ Original Height} = \frac{h_o - h_f}{h_o} \times 100$$

$$\% \text{ Deflection} = \frac{h_o - h_s}{h_o - h_s} \times 100.$$

where: h_o = original height

h_f = final height

h_s = height of spacer

In some of the GSA specifications you will find the terms

$$\frac{T_o - T_{30}}{T_o - T_s} \times 100. \quad \text{The RMA Foam Specification Guide states that}$$

The maximum compression set is based upon percentage of original height should be no greater than 10% and when based upon the spacer height shall be no greater than 20%. These limits are for cored and uncured materials.

VINYL FOAMS - TEST SPECIMENS - Vinyl foams are tested in a slightly different manner, taking into account the slowness of their response to a static load. The specimens may be of any convenient size with parallel top and bottom surfaces which shall be at right angles to the side surfaces. The specimen may be round or rectangular. The minimum dimensions across the top shall be at least one time the thickness and at least one square inch in area. The minimum thickness shall be one-half inch. This smaller size permits the testing of vinyl foams used for applications other than seating, such as crash pad or "A" post applications. The original height is measured accurately to 0.001 inch and the specimen is placed between plates in a clamping device and compressed to 50% of the original height. The specimen is exposed for 22 hours at 70°C in a hot air oven, released from the clamping device, returned immediately to the oven and allowed to recover for 2 hours. The sample is then removed from the oven and allowed to come to equilibrium for one hour at room temperature. The

compression set calculations are identical to these used for latex foam.

URETHANE FOAMS - BOTH SLAB AND MOLDED - Urethane foams both slab and molded are also tested for compression set in the same manner as latex and vinyl foams. The method consists of deflecting the foam specimens under specific conditions of time and temperature and noting the effect on the thickness of the specimen. Compression deflection devised consists of two or more flat plates arranged parallel to each other and held in place by bolts or clamps with a space between the plates adjustable to the required deflection by means of spacers. The test specimen shall have parallel top and bottom surfaces and essentially perpendicular sides. This is not always possible on molded contour pads. The specimen from uncured stock shall be 2 x 2 x 1 inch less otherwise specified. Specimens of less than one inch in thickness shall be plied without the use of cement to the 1 inch mark. Specimens from cured stock shall be such a size that the coring does not appreciably effect the results, and they shall have a minimum top surface area of at least 16 square inches. The thickness shall be no greater than 75% of the minimum top dimensions. Three specimens are usually tested. After the

specimens have been conditioned for at least 12 hours in the CTH room, they are measured to the nearest 0.001 inch. The specimens are placed in the jig and deflected to either $50\% \pm 1$ or $90\% \pm 1$, depending upon the values called for in the specification. The 90% deflection in some automotive specifications is referred to as a crush recovery test. Within 15 minutes place the deflected specimens in a mechanically circulated air oven for a period of 22 hours. Remove the specimens immediately from the apparatus -- do not let them cool in a compressed position -- and measure to the nearest 0.001 inch. The recovery period shall be $30 - 0 + 10$ minutes. The compression set may be calculated based upon the original thickness or expressed as a percentage of the original deflection. The usual value seen in specifications is 10 or 15% for the 50% deflection and 15 to 20% for the 90% deflection when calculated on the basis of the original deflection. Several precautions should be exercised in running this test, they include the following:

1. The jig shall have sufficient smoothness of surface so as not to interfere with the test; 50 microinches is acceptable.
2. The jig shall not be deflected by the clamping procedure.
3. If there is a tendency for the molded pads, which may have a residual wax, to stick to the platens, it may be

necessary to dust the foam with a talcum or mica, or to use a sheet of cellophane between the platen and the foam itself. There is a tendency of some molded foams to have edge sticking. Consequently, the sample when it is released from the jig and allowed to recover will be wedge shaped. This type of test specimen is difficult to measure and it is often discarded as being unsuitable for determination.

A SPI Comparison Testing Study (March 1, 1966) would seem to indicate that additional studies are needed for medium density filled foams.

TABLE IV

COMPRESSION SET STUDY - FILLED FOAMS

<u>Density</u>	<u>Company</u>	<u>Foam A</u>		<u>Foam B</u>		<u>Foam C</u>	
		<u>50%</u>	<u>90%</u>	<u>50%</u>	<u>90%</u>	<u>50%</u>	<u>90%</u>
3.0 to 3.5	1	2.7	31.0	3.8	6.5	2.7	22.4
	2	6.0	6.1	10.0	42/ 90	4.1	4.7
	3	4.8	6.5	5.1	6.0	2.2	3.5
	4	3.7	82.0	4.8	76.0	2.8	16.3
	5	---	5.7	---	---	---	5.3
	6	3.2	60.0	4.7	40.9	2.9	8.3
	7	5.1	55.0	8.4	10.0	5.8	6.2
	8	5.4	8.7	6.2	6.2	5.0	5.4

HUMID AGING

The humid aging test consists of exposing a specimen of flexible foam to elevated temperature and humidity and determining the effect on the properties. The test originally consisted of exposing a specimen in a low pressure steam autoclave for 3 hours at 220°F. With the development of one-shot polyethers, this test proved to be too mild and the conditions were changed to 5 hours at 250°F. The automotive humid aging test is 7 days at 190 to 195°F in a closed container.

In ASTM for urethanes, two conditions are given:

Condition A - 3 hours at 220°F for polyesters

Condition B - 5 hours at 250°F for polyethers.

The test specimens are dried for 3 hours per inch of thickness in a mechanical convection dry air oven. The specimen is next conditioned for at least 2 and not more than 24 hours under standard conditions of temperature and humidity.

The autoclave is filled with fresh distilled water to the 2 inch level, set at the desired temperature and the water is allowed to come to a boil. The basket containing the samples which are not allowed to touch one another is placed in the autoclave, the cover is secured and the steam is allowed to escape for

two minutes. The steam valve is closed and this starts the beginning of the test. After the exposure period, the heat is turned off and the steam is released. The specimens are dried for 3 hours per inch of thickness in a mechanically convected oven. The samples are then allowed to come to equilibrium in the CTH room for at least 2 and no more than 24 hours. The specimens are tested for compression load and compression set.

In 1961 and 1962 the SPI conducted an extensive round robin on the humid aging test. They studied different conditions of time and exposure as well as different tests such as tensile, elongation and tear. The report was given on August 8, 1962 and recommended the two conditions, A and B, but because of the poor agreement between laboratories on tensile and tear results, only the compression set and compression load tests were included in the revision of D-1564. Typical results obtained in this study are given in Table V.

The humid aging test is part of most specifications and is also used to determine color fastness, the retention of flame retardants and sterilizability. The test is very specific as to the drying times, but a study is still required to determine if these conditions are adequate for filled foams.

TABLE V
HUMID AGED STUDY

<u>Company</u>	Tensile Original psi.	<u>% Change</u>				
		<u>220°F</u>			<u>250°F</u>	
		<u>3 hrs.</u>	<u>6 hrs.</u>	<u>22 hrs.</u>	<u>5 hrs.</u>	<u>22 hrs.</u>
A	12.7	+10.2	+9.1	+7.9	-18.1	-23.6
B	12.2	+6.5	+10	+7.4	+16.3	-9.8
C	15.1	-0.7	+1.0	-0.7	+2.0	-15.0
D	18.5	-0.5	-1.1	-8.1	-4.9	-37.3
E	17.4	-6.9	+2.3	-4.6	-0.6	-40.0
F	16.3	+1.8	-2.5	-8.0	+1.8	0.0

Compression Set = 90% - 22 Hours, % Change

A	4.9	10.3	16.3	18.3	22.4	31.6
B	4.8	132	52.0	198	222	279
C	5.7	+5.3	5.4	216	224	200
D	2.6	7.5	11.3	392	304	24.0
E	7.0	5.7	24.3	51.2	50.0	47.0
F	4.7	162	256	360	416	130

HEAT AGING TESTS

The heat aging test appears in one form or another in almost all the flexible foam specifications and test methods. The dry heat aging test consists of exposing flexible foams in an air circulating oven and observing the effect on some particular property. Latex foams are heat aged for 22 hours at 100°C and a change in load deflection values are measured. Vinyl foams are tested according to their hardnesses.

For softer foams the indentation sample is 12 x 12 x 1, while for the hard V0 grade compression deflection is measured. For the harder foam the sample size is reduced to 1.129 inches in diameter or exactly 1 square inch. The foams are exposed for 22 hours at 212°F and they are allowed to come to equilibrium in a room for 22 hours before the final test. In the GSA mattress specification the foams are exposed at only 70°C (158°F) for 166 hours and the sample is then allowed to come to equilibrium for 16 hours before the final test. ASTM D-1564 and D-2406 specify that the foam is exposed for 22 hours at $140^{\circ} \pm 2^{\circ}\text{C}$ (284°F). The foam is allowed to recover for 12 hours at standard conditioning and then tested for tensile and elongation. It is therefore apparent that the heat aging values reported on one type of material

are not comparable to values reported for another type of seating or flexible material. For urethane foams, both flexible and semi-rigid, the test consists of exposing a flexible foam specimen in an air circulating oven and observing the effect on tensile properties of the foam. To assure that the oven is operating properly, a continuous recorder is recommended. The tensile dumbbells are died from a slab stock a half inch thick and the gage is measured. The samples are then suspended in a container of sufficient size so that the specimens do not touch one another or the container. A small vent hole, usually an eighth of an inch in diameter is placed in the top of the container. A tin plate one-gallon can has been found suitable. It is specified that a separate container be used for each type of sample to prevent possible contaminating of the other samples. The specimens are usually suspended on a fine wire mounted at the top of the container. In many laboratories where the same foam is being tested over and over again, a large circulating oven is used and the samples are suspended by bent paper clips or mounted on racks. Three specimens constitute a test. The procedure is simple, the specimens are measured, suspended in the container and placed in the oven for 22 hours. The samples are then

removed and placed in the constant humidity room for at least 12 hours before the final determinations are made. The percent change in strength properties are calculated. Many laboratories will cut and expose five specimens and test only three unless one of the three specimens falls outside of a normal reproducibility limit, and then the other two are tested. In this particular case, the average of all five specimens is reported.

In the latex and vinyl foam specifications, the heat aging properties shall not vary more than a plus or minus 20 from the original value. Urethane foams are also specified as usually a plus or minus variation from the original. Upon heat aging the tensile properties of a foam may increase or decrease, depending upon the type of foam. An undercured molded foam will usually increase in both tensile and elongation upon heat aging. If the foam is already cured and does not contain any heat stabilizing materials, it is not uncommon to find that the tensile will increase as the elongation decreases. Since the properties of the tensile measurement are relatively low such as 12 psi., it is important that this measurement be made as precisely as possible so as to assure that you do not eliminate a foam because of careless laboratory measuring techniques. Some foams which have plasticizers in them are also measured for the loss of this plasticizing

effect upon heat aging. These foams may remain the same color or it is not uncommon to see that they will darken upon heat aging. Foams containing organic flame retardants may also darken on heat ageing. This test is interesting and significant and it is not uncommon that many laboratories, when introducing a new polymer will expose the foam for tensile, elongation, tear, compression set and compression load so as to reassure that all the properties as measured by these separate tests maintain reasonable values.

HARDNESS

Foams for seating and bedding applications are sold on the basis of hardness. Hardness is measured by an indentation test. The indentation test and hardness grades for latex foams are covered in ASTM D-1055, this test is also called the RMA (Rubber Manufacturers Association) test. The indentation test for urethane foams is described in ASTM D-1564 and D-2406. There are many factors that can effect the results obtained by these tests. They are the type of preflexing, specimen size and thickness, the rate of loading, the presence or absence of molded skins, cut surfaces, coring if any and type, density, cell size, position in the bun and temperature and humidity of the testing room.

ILD TEST - The indentation load deflection test consists of measuring the load necessary to produce a 25 and 65% deflection. These loads are known as ILD values. The apparatus (Figure 5) consists of a flat, circular, 50 sq. in. indenter foot which is attached to the load measuring device by means of a swivel joint. This, of course, is necessary for contoured and molded pads. The specimen plate is level and horizontal which is perforated with quarter inch holes on three-quarter inch centers to allow the rapid escape of air during the test. The rate of loading is specified at 1 to 15 inches per minute. Many laboratories have arbitrarily decided upon 2 inches per minute and this also conforms to the rate required by several of the automotive specifications. The specimen size is a minimum of 15 by 15 with a minimum thickness of $3/4$ inch. Specimens of less than $3/4$ inch should be plied up without cement to at least this thickness. The test procedure has been written out in great detail and calls for the entire specimen to be preflexed twice to 70 to 80% of its nominal thickness. The specimen is then allowed to rest for a period of 10 ± 5 minutes. The specimen is placed on the flat horizontal perforated plate. If the foam is cored or honeycombed, this surface shall be faced down. Whenever practical, the indentation shall be made

at the center of the specimen. This is particularly true when the specimen is an entire cushion or mattress. The thickness of the foam is measured by bringing the indenter foot into contact with the specimen and applying a load of one pound. For a 50 sq. in. indenter foot, this corresponds to a very minor load of 0.02 pounds/sq.in. It also enables the swivel foot to level itself in relation to the foam in case the top and bottom surfaces are not exactly parallel or if the foam is contoured. The foam is then compressed to 25% of its thickness and the load is measured after a one minute wait. Without removing the specimen, the deflection is increased to 50 and later to 65% and again the load is observed after a one minute drift period. The precision of this test is within a $\pm 5\%$ at the 25% deflection and a $\pm 10\%$ at the 65% deflection.

The two methods, that is for latex and urethane foams, differ merely in the type of preflexing and the waiting period. In the manufacture of latex foams, it is a common practice to wash and squeeze out some of the materials used in manufacturing and then to dry the foam. This operation fractures and opens all cells. In urethane foams it was not uncommon in the early days to have foams that had 15 to 30% closed cells; therefore, it was necessary to crush the foams between

reollers or plates to open these cells. This is still part of the ASTM procedure for urethane foams, that is to crush the foams to make sure that there are no closed cells. The big difference between the two tests is in the reading of the values; for the rubber foams the ILD or RMA value is read 5 seconds after the crosshead reaches its proper deflection, while for urethane foams, this reading is made one minute after proper deflection is reached. The load deflection properties of cellular materials have been studied quite extensively and this type of loading curve becomes specific for almost each type of foam. The ILD test has been under almost continuous study by either the SPI or the ASTM since 1959. With so many variables effecting the final value, each variable had to be studied in order to tighten up the procedure to assure reproducible results. Since latex foam is not appreciably effected by these variables, such as type of preflexing, humidity, etc., this discussion is pointed mainly at the urethanes.

EFFECT OF PREFLEXING - The 1959 version of D-1564 gave the researcher the option of preflexing the foam twice between parallel plates or rollers to crush any closed cells. With the development of new technology the need for crushing was lessened

and the preflexing was done with the indenter foot. The hardness value of 65% deflection increased when the indenter foot was used (Table VI); but when the foam was tested for fatigue properties the problem became concerning because of the high fatigue values that were reported.

TABLE VI

SPI PREFLEXING STUDY - OCTOBER 1963

<u>Determination</u>	<u>Preflex Method</u>		
	<u>Plate</u>	<u>Roller</u>	<u>Ind. Foot</u>
25% ILD	32.5	33.1	31.2
50% ILD	44.3	46.3	44.5
65% ILD	55.4	57.7	59.1
25% ILD Return	19.9	19.6	20.6
Modulus (Sag Factor)	1.70	1.74	1.89
% Hysteresis Loss	38.9	40.9	34.3
Guide Factor	22.7	23.1	21.5

Sample Size 15 x 15 x 4 inches.

To sell foam on the basis of high ILD values was one thing, but to have it rejected for high fatigue losses was something else. Latex foam, because of its manufacturing procedure, already had

a stabilized hardness and since large quantities of urethane foams are sold to slitters, there was no practical way for the foamer to preflex or crush these large buns. The concept of an equalized ILD took hold and two Subcommittees of the SPI Technical Group arrived at about the same solution. The Indentation Load Deflection Committee decided that six preflexes would be sufficient to obtain reproducible values.

TABLE VII

SPI PREFLEXING STUDY - DECEMBER 1, 1965

<u>Cycle No.</u>	<u>ILD</u>		
	<u>25%</u>	<u>50%</u>	<u>65%</u>
1	73	89	110
2	44	62	88
3	41	59	85
4	40	58	83
5	39	57	82
6	39	56	82

Crosshead speed 2"/min.

The Fatigue Subcommittee, in order to obtain equalized ILD values, decided on 10 preflexes. After all, it is still the same foam. The hardness values are now lower and the fatigue

losses are now equal to or better than latex foams.

HUMIDITY - Summer softening plagued the industry for many years. In the dry, cold weather a foam would be firm, while soft in the warm moist season. With the glass transition temperature of urethane foams down below 50°C, studies have shown that humidity can and does lower the hardness of the foam. Moisture may act as a plasticizer in summer, resulting in softer foams.

It is therefore essential for referee purposes that the foam be tested at $23 \pm 1^{\circ}\text{C}$ ($73.4 \pm 2^{\circ}\text{F}$) and in an atmosphere of $50 \pm 2\%$ relative humidity. It is also recommended that foams be conditioned at least 12 hours in the CTH room before testing and for good uniform results that the foam be at least 96 hours old. Obviously, it is essential that the foams be stored in an undeformed and undistorted position. In molded foams, the colder the surface of the mold the thicker the skin, hence, the higher the hardness. Molded foams, therefore, should be tested on the top seating surface which is usually the bottom of the mold.

Just before the foam is completely gelled, the windows of the cells open and the foam drops a fraction of an inch in height. This along with a natural density spread will result in foams of varying

hardness throughout a bun. The lower hardness is near the top, with the firmer foam near the bottom.

HYSTERESIS - Hysteresis measurement, although not a part of any formal foam test requirements, is often used to yield additional information. After sufficient preflexes to obtain an equilibrium ILD, the specimen is deflected to 75% of its height at a rate of 2 inches per minute. The hysteresis measurement can be made with an Instron equipped with an integrater. The loading and unloading curves can also be measured with a planimeter. Some laboratories use the simple method of cutting the loading and unloading curves out of the chart paper and weighing them on an analytical balance. Hysteresis is simply calculated by determining the percentage difference between the loading and unloading curves. This often times is subtracted from 100 which would be the theoretical amount if the entire unloading curve equaled the loading curve and this is often referred to as a theoretical resilience value. The 25% ILD loading and unloading values are required by some of the automotive specifications. This simply is a very rapid way of arriving at an indication of the hysteresis of the foam.

Figure 6 shows some typical loading curves for some seating materials. No. 1 is a tempered metal coil spring, No. 2 is latex foam, No. 3 is a polyester urethane, and No. 4 is a polyether urethane. Many attempts have been made to describe the loading and unloading curve in simple terms. The sag factor is the ratio of the 65% to the 25% ILD value. The guide factor is the ratio of the 25% ILD value to the density. A sag factor of 1.8 is considered normal for most urethane foams. A sag factor of 2 is considered exceptional. Many of the specifications will simply give the 25% ILD value and then to obtain the 65% ILD value you multiply by 1.8.

In the British standard 3379-1861, several other concepts are used to describe in part this loading and unloading curve.

Indentation Modulus

$$I_m = \frac{H - L_{20}}{20}$$

where: H = Indentation hardness index = 40% ILD

L_{20} = Load at 20% indentation.

Modulus Irregularity Factor

$$MIF = 2L_{20} = H$$

In these calculations it is assumed that the values between zero and 40% ILD are for all practical purposes a straight line.

TABLE VIII

BRITISH STANDARDS 3379-1861,

INDENTATION MODULUS & MODULUS IRREGULARITY FACTOR

<u>Determination</u>	<u>Latex</u>	<u>Slab Polyether</u>	<u>Molded</u>	<u>Filled</u>
L ₂₀	7.34	11.64	6.94	8.75
H	9.98	12.25	8.80	11.00
Im	0.132	0.031	0.093	0.113
MIF	4.7	11.03	5.08	6.5

THE RATE OF DRIFT - The one minute drift period required in the ASTM urethane specimens assumes that all foams have the identical response to a loading force and that they reach an equilibrium value in 1 minute and that this creep then levels off quickly. This decay in load expressed as a percentage yields some interesting data. Percent drift is equal to the instantaneous value minus the 1 minute value over the instantaneous value times 100. As you would expect, this is not constant per each percentage of deflection and shows that the foam does not respond equally at all levels of loading and that creep is therefore dependent upon the loading phenomena (Table IX).

TABLE IX

PERCENT LOAD DRIFT AND RESILIENCE

<u>Determination</u>	<u>Latex</u>	<u>Slab</u>	<u>Molded</u>	<u>Filled</u>
CLD ₂₀	6.3	12.0	11.4	8.9
CLD ₄₀	5.7	10.5	10.9	8.6
Resilience	52.9	44.7	45.8	33.2

CLD₂₀ = 20% deflection

CLD₄₀ = 40% deflection

$$\% \text{ Drift} = \frac{\text{CLD}_{20}\text{-ins.} - \text{CLD}_{20}\text{-1. min.}}{\text{CLD}_{20}\text{-ins.}} \times 100$$

IRGL TEST - A second method for determining foam hardness by indentation tests is the Indentation Residual Gage Test. This is called the IRGL, and measures the indentation to a specific load. The automotive industry is particularly interested in determining how thick the padding or cushioning is under an average person. Eye level is related to residual seat height under load and this is an important factor for drivers ease and operation and for full view of the highway. The requirements for IRGL are identical with those for ILD. The specimen size is the same, 15 by 15 by at least 3/4". The flat indenter foot

has the same area and the perforated plate has the 1/4" holes on 3/4" centers. The specimen is preflexed twice under 75 pounds load. The rest period is 10 ± 5 minutes. If this portion of the test is run according to the Society of Automotive Industry, the rest period is 5 ± 1 minute. Since the preflexing was done at 8 inches a minute, the speed is then changed to the 2 inches per minute to perform the rest of the operation. The height is then determined under a 1 pound load. A 25 pound load is applied and the thickness is measured after 1 minute. Without removing the specimen, the load is increased to 50 pounds and the thickness or residual gage is measured after 1 minute. Three values are reported; the thickness of the sample under a 1 pound load, the residual gage under 25 and 50 pounds load. The 25 pound load does not penetrate very far into the foam, so for most values the 50 pound loaded value is specified in Buyers Guide and for fatigue measurements.

(Fig. 7). The IRGL test can be run on an Instron or other electronic weighing machines, but the Burke Porter testing machine was developed specifically for this measurement. The Burke Porter is a machine that is simple to operate, it is rugged, dependable and precise, and it sells for under \$3,000. It can

be used at the end of a production line by untrained personnel and it will perform with an amazing precision. The IRGL test, like the ILD test, has several limitations and these include inconvertibility of the values. The IRGL cannot be related to the ILD and both tests are dependent upon sample size and thickness. If you know the 4 inch value you cannot predict the 2 inch value and if you know the value for a 15 by 15 specimen you cannot predict what the value will be for a 10 by 10 or 20 by 20 specimen. The thicker the specimen the more support the undeflected portion will give. This hammocking effect is more pronounced with molded parts because of the density of the skin. As the sample becomes thicker, say from 2 to 3 to 4 inches, the distance of the area not being deflected approaches that of the thickness of the material giving a poor sample configuration and size. The guard ring method appears to solve many of these problems associated with ILD and IRGL measurements. The guard ring, or K-ring as it was previously known, operates on the simple fact that compression load deflection values in psi. are independent of the sample thickness provided the height of the specimen does not exceed the surface dimensions of the indenter. This method was developed by Kay Brothers Limited, the foamers in England and is now being considered by ASTM as a possible method. The procedure is identical to the

ILD test except that the sample can be any size or thickness. When the sample size is smaller than the indenter's area, the value is reported in psi. and this is equivalent to a compression deflection value. Table X shows the results obtained on the same foam using the ILD and guard ring.

TABLE X

KAY RING - HAMPDEN TEST EQUIPMENT, LTD.

RUGBY WARWICKSHIRE, ENGLAND

<u>Thickness, in.</u>	<u>ILD</u>			<u>Kay Ring</u>		
	<u>25%</u>	<u>50%</u>	<u>65%</u>	<u>25%</u>	<u>50%</u>	<u>65%</u>
1	7.1	8.6	12.5	6.3	7.4	11.0
2	8.4	10.2	14.4	6.2	7.3	10.8
3	9.3	12.1	16.9	6.7	7.8	11.3
4	10.1	13.4	18.6	6.5	7.9	11.3
1	23.2	31.3	49.0	22.8	28.0	42.0
2	24.8	35.7	54.9	20.7	26.0	41.0
3	31.2	47.0	70.8	23.6	29.0	44.0
4	32.3	49.6	72.4	25.0	30.0	44.0

COMPRESSION LOAD DEFLECTION TEST - The CLD test consists of measuring the load required to produce a 25% deflection over the entire top area of the foam specimen. The apparatus consists

of a flat compression foot larger than the specimen to be tested. It is connected to a load measuring device and mounted in such a manner that the product or specimen can be deflected at a speed of 1 to 15 inches per minute. The horizontal level perforated plate with $1/4$ " holes on $3/4$ " centers, these holes allow for the rapid escape of air during the test. The specimen shall have parallel top and bottom surfaces with essentially vertical sides. The thickness of the specimen shall be no greater than 75% of the minimum top dimension. The specimen from uncored stock shall be a minimum of 4 sq. in. in area and a minimum thickness of $3/4$ ". Specimens less than $3/4$ " shall be plied up without the use of cement to the minimum thickness. Specimens from cored stock shall be of such a size that the coring does not appreciably effect the compression value, normally this would depend upon the size of the coring, larger the coring the larger the size of the sample. Three specimens per sample are usually tested and the average value is recorded. The specimens can be cut with a scalloped blade saw or die cut or if possible, even cut with a 4" hole saw. The test procedure is simple, the sample is preflexed twice, 75 to 80% of its original thickness and the specimen is allowed to rest for a period of 10 ± 5 minutes. The specimen is placed centrally in line of the axel

load on the supporting plate of the apparatus. In case the product has one side honeycombed or cored, this, of course, rests on the perforated plate. Bring the indenter foot into contact with the specimen and determine the thickness after applying a preload of 0.02 psi. of the specimen area. This at times is a very tedious operation and some laboratories will simply use a 1 inch diameter pressure foot on a dial gage to determine the thickness. The specimen is then compressed 25% of this thickness and final load observed after 1 minute. Then, in many specifications, the 50 and 65% compression deflection values are determined. For super soft foams a reduction of pressure on the compression foot shall be allowed. All CLD values are in pounds per square inch. Compression deflection for the V0 grade of vinyls is similar to the flexible urethanes, except that the sample size is 1 square inch surface area or 1.129" in diameter, and the rate of testing is 1/2 the 20 inches per minute. The 25% deflection is called for and the final load in pounds is observed 60 seconds after the deflection is reached. Compression deflection tests are also specified for sponge and cellular rubber products according to the D-1056. In each and every case the smaller size sample permits

the specimen to be subjected to other environmental conditions such as humid aging and heat aging or low temperature measurements. This of course, is not possible with the larger specimens of 15 by 15 size used for the indentation load deflection test.

FUNCTIONAL LIFE TEST

Fatigue testing attempts to measure resistance of a cushioning or bedding material to repeated flexing or at elevated temperature, a 180° fold under static conditions.

FLEXING TESTS FOR LATEX FOAMS - The flexing test consists of subjecting the test specimens to repeated compression and noting the effect on the cellular structure. The test specimen consists of the entire product sample or a suitable portion of it as agreed upon by the manufacturer and the purchaser. The full thickness of the product shall be used. In mattress testing and pillow testing, this is sometimes reduced to a reasonable thickness that the fatigue tester can handle. The test specimen shall be placed centrally on a stationary plate of the flexing machine (Figure 8). The flexing plate of the machine shall be at least 1/4" larger on each side than the specimen being tested. Where the product being tested has one side cored or honeycombed, this face shall rest on the perforated

plate. For products having an indentation value of less than 1.34 psi., the amplitude of the compression and the decompression shall be 50% of the original thickness. For products having an indentation value higher than 1.34 psi., the amplitude shall be 25% of the original thickness. The machine shall be reciprocate at 60 cycles per minute and the total number of flexes recorded. The test usually consists of repeated flexings of 250,000 cycles. Failure of the specimen is evidenced by physical breakdown of the cellular structure and is determined by visual examination and comparison with an unflexed specimen. Besides the actual visual examination, the original height under 1 pound load is measured as well as the 25% ILD value is measured after fatiguing and the percentages are calculated as percent loss in properties under these two measurements. This test is often called the Bouncing Betty by people working in the laborabory. In passing, it is interesting to note that this is, for the most part, a very mild fatigue test. It recognizes two grades of foam. These hardnesses are based upon a 25% deflection value, on a 12 by 12 sample where the value is then converted from the 50 sq. in. to pounds per square inch value. This, as we know today,

is not exactly correct. The latex foam document was written many years ago, 18 to be exact and it is probably now in need of a good revision.

The static fatigue test consists of bending or folding a piece of foam 180° and subjecting to static conditions at elevated temperatures. The specimen of a latex foam measures 4 by 9 inches and shall be bent parallel to the 4 inch dimension to an angle 180° between two compression plates and placed in an oven at 158°F for 22 hours. The opening of the space between the two plates shall be twice the thickness of the unfolded specimens. The folded edge of the specimen should not extend beyond the edge of the compression apparatus. If skin is present on the sample, it shall be folded out for testing. Upon removal from the oven the sample is released from the jig and when lain flat it shall show no evidence of cracking along the folded edge.

VINYL FOAMS - DYNAMIC FLEXING TEST - The flexing test consists of subjecting the test specimens to repeated compression and noting the effect on the structure. The apparatus is identical to the Bouncing Betty. The top plate shall be suitably

connected to a recipricating mechanism which will oscillate at the rate of 60 times per minute in the direction normal to the surface of the plates. The bottom shall be stationary and perforated with 1/4" holes on 3/4" centers to allow for the rapid escape of air. The machine must be so designed that the space between the two plates can be adjusted to the height of the specimen. The stroke of the machine shall be at least 50% of the specimen thickness. The specimen shall have parallel upper and lower surfaces and be at least 12 by 12 inches. The specimen is measured for thickness according to the standard ILD indentation load procedure. For products having indentation load values of less than 67 pounds per 50 sq.in. the amplitude of the compression and decompression shall be 50% of the original thickness. For products having indentation load deflection values greater than 67 pounds per 50 sq.in., the amplitude shall be 25% of the original thickness. The machine shall oscillate 60 cycles per minute and the test shall consist of 250,000 flexes. At the completion of the flexing, the sample is removed from the apparatus and allowed to rest for 24 hours. It is then examined carefully for visual breakdown and by comparison with an unflexed specimen. The height and the 25% ILD

can then be determined according to the standard procedure. The set, based upon the original height is calculated according to standard percentage loss calculations.

The static fatigue test for vinyl foams is identical to that of latex in that it determines the ability of the material to withstand a 180° fold under static conditions at elevated temperatures. In the vinyl test the specimens are usually cut in strips 2 inches by 10 inches by not more than 1 inch thick. They may have skin on the 2 or 10 inch surface. The 2 by 10 inch specimen of vinyl foam is bent parallel to the 2 inch dimension to an angle of 180° and placed between compression plates and then placed in the circulating oven at 70°C for 22 hours. The opening of the plates shall be equal to twice the thickness of the unfolded specimen. The folded edge of the specimen shall not extend beyond the edge of the compression plates. Fold the skin side, if present, outward for testing. The specimen shall show no cracks at the end of the test. In latex and vinyl foams the two fatigue tests, the dynamic flexing test and 180° static fatigue test, can be used to separate foams of varying qualities, and they have found widespread use for this determination.

URETHANE FOAM - With the introduction of urethane foams there was renewed interest in fatigue testing. It was only natural that the first urethane fatigue test should be based upon the Bouncing Betty variety. Other methods and ideas were tried and there are in ASTM D-1564 six procedures listed with six variables. They include the Bouncing Betty type of test under constant deflection and under constant load. The static fatigue test under constant deflection or constant load (Fig. 9). The roller shear fatigue test under constant deflection or constant load (Fig. 10), and a rotating plate test under constant deflection. The purpose of all these different fatigue tests was to determine first the loss of load bearing properties, second loss in thickness and third, structural breakdown by visual examination. The tests listed in this document recognize the existence of a large number of tests currently in use. Some of them for actual production performance testing and others for polymer characterization work. The measurements of load, thickness, calculation of results and reporting of the data is the same regardless of the type of fatigue used. Only the apparatus, the specimen size and the actual test technique vary. It was recognized that further industrial experience would reduce the number of test methods to a minimum. Subsequent years of experience have shown that this is to be true.

The test consists of one specimen, the height and hardness values are determined according to the indentation load deflection test, the indentation residual gage test or the compression load deflection test. Thirty minutes after fatigue is completed, the final results are measured. This 30 minutes recognizes that these materials do recover and that an equilibrium time is necessary. Research has shown that maximum recovery will take place for most of the test procedures within the first half hour. If the loss in thickness is above 10% the load loss would be indeterminant and only the thickness loss would be reported. A detailed discussion of each one of the test procedures will serve as the basis for further discussion on the meaning of the results.

Static Fatigue - The procedure A is a static deflection test.

The apparatus consists of two parallel plates that can be made out of wood, metal or any rigid material which can be used to produce a constant deflection on the specimens. The plates are usually 20 inches by 20 inches and spacer bars are used to adjust the deflection to 75%. The test specimen usually consists of only one specimen measuring 15 by 15 by the desired thickness.

The specimen is placed between the parallel plates and the spacer bars are adjusted to produce a 75% deflection. The plates are clamped and held at 75% deflection for 17 hours at 23 ± 1.1 °C and 50% relative humidity. Upon the completion of the time period the sample is removed and allowed to come to equilibrium in the CTH room in an undeflected position for 30 minutes. It is then immediately tested according to the original determinations and the percentage loss calculated. The static fatigue is also known as the du Pont fatigue method. A great deal of effort has been expended by duPont and other companies in the development of this test. It recognizes that foams when subjected to constant deflection at room temperature will recover. The recovery will be based upon many parameters, and properties. It is recognized that this is not a permanent damage to the foam, it is similar to placing a very heavy calculator or suitcase or trunk on a cushion and then leaving it there for a considerable period of time. It was interesting to note that in the early development of fatigue testing, results obtained from static fatigue correlated very well with performance testing, based upon the Belgium Block Road Test. At least it correlated in that the percentages loss were almost identical. The

static fatigue test can also be run under constant load as has been done experimentally in many labs, but it is now not part of any standard specification.

Fixed Amplitude - Bouncing Betty - Procedure C of 1564 is identical to the Bouncing Betty procedure listed in the latex and vinyl test procedures. The apparatus consists of having a machine with parallel plates, one which moves with respect to the other to produce a uniform deflection of the specimen. The bottom plate is perforated to 1/4" holes on 3/4" centers to enable the gas to escape. The flexing plate of the machine shall be at least 1/4" larger on each side than the specimen being tested. The machine operates at 60 cycles per minute. One specimen is tested and it measures 15 by 15 by at least 3/4 inch in thickness. The plate is adjusted in position so that the amplitude of the flexing with respect to the specimen shall be 75% of the original thickness. The specimen is placed on the flexing machine and subjected to 250,000 flexes. Thirty minutes after the test is completed the specimen is measured to thickness and for load deflection as was done in the original determination. This test has been modified by Chrysler Corporation to a CLD specimen size. The sample is cut, original hardness determined, placed in the

flexing machine and the amplitude of the flexing is adjusted to either 85 or 90% of the specimen's thickness. In the newer specifications at Chrysler it calls for the 90%. The number of cycles is therefore reduced from 1/4 of a million down to 100,000 cycles. At 60 cycles per minute this takes between 26 and 27 hours and facilitates a rapid screening of materials.

Roller Shear - The roller shear method is called Procedure D. This is also called the Ford Roller Shear Test. The apparatus consists of a roller 18" long and 3" in diameter which is mounted in an off-set position at 15° with a suitable means of adjustment for specific deflection or load on the specimen. The test is conducted at a rate of 28 cycles per minute back and forth across the sample. The specimen measures 15 by 15 by the desired thickness. A three inch wide strip of cotton sheeting is bonded to the sides of the specimen. Two inches is allowed to extend beyond the edges of the test specimen so that it can be securely held on the base plate of the tester with retainer metal straps. The roller is adjusted to obtain a 65% deflection and this is based upon the 1 pound preload height. The specimen is flexed 20,000 flexes or 40,000 cycles. One-half hour after the completion of the test, the sample is measured in the exact manner as originally and the percent losses are calculated.

Procedure E is a Ford Test at constant load (Fig. 10). This operation is identical to the constant deflection method.

In the development of this test the load was usually applied to give an original 65% deflection and as the sample softened this deflection increased and the roller went deeper into the foam. Nowadays, the procedure simply calls for a constant load of 37-1/2 pounds on a 15 by 15 sample and if a smaller specimen such as 15 by 12 is used, the load is reduced to 30 pounds on the roller shear.

As in the other test procedures, 30 minutes after the completion of the test, the values are determined and the percent loss in height and load bearing properties are calculated. Procedure F of ASTM 1564 consisted of a rotating plate driven by a constant speed motor in which the foam sheet covered by canvas was placed. This method was promulgated by Dr. Samuel Steingeiser of Mobay Chemical, and consequently has been referred to as the Mobay Shear Test. This test, while very useful in the laboratory, has not received much recognition by the commercial users. The basic limitation of the test is that the sample thickness was less than 1 inch, while 1/4" being the normal thickness tested. For such thin sections it was extremely difficult

to get precise measurements on anything but the most sophisticated type of electronic weighing equipment.

LOW TEMPERATURE TESTING OF FLEXIBLE MATERIALS - Many of the automotive specifications have a low temperature flexibility requirement. These tests are usually one of three types: (1) bending of a long rectangular column of foam around a mandrel, (2) compression deflection at low temperature according to the sponge test method, ASTM D-1056 and (3) ILD determinations at either -20 or -40°. The details for each test are about the same. The sample is exposed, usually for 1 hour per inch of thickness at -20 or -40°. In the case of the bending test, when the sample is bent around a mandrel there should be no cracking or breaking. The compression deflection test, the sample is also tested in an environmental chamber and the hardness is not allowed to increase over a given percentage. The indentation measurement is more difficult to make. The sample size is usually 15 by 15 or in some cases 12 by 12. The original hardness is determined by the ILD method. The sample is then exposed for 1 hour per inch of thickness to the given temperature and it is then immediately tested at the same temperature. This constitutes part of the problem. There are probably only 1 or

2 Instrons or other test equipment in the United States capable of taking this large a sample. So even though the test method usually states that the indenter foot and the base plate shall be at -20, to comply with this requirement they would have the base plate and indenter foot in the refrigerator and very rapidly run to their testing equipment, set it all up and attempt to run the determination. Most of the automotive specifications will simply permit the doubling of the hardness at the specified temperature. The one danger, of course, is that some humidity may get into the foam and at this temperature, ice crystals would form and give erroneous values. Foams with very high filler concentrations may be stiff in themselves, and may exhibit low elongation at room temperature and may have difficulty passing the low temperature bend test. Not because the polymer had gone through a glass transition or crystallinity stage, simply because of high filler loading and low elongation.

LOW TEMPERATURE TESTS - LATEX FOAMS - A cylinder of foam 1.129 inches in diameter is used for this test. The minimum thickness shall be $3/4$ ". The specimen is first dried in a desiccator for not less than 16 hours. The compression deflection of the specimen is first measured at room temperature and the load in pounds per square inch necessary to obtain a 25% deflection is recorded.

The specimen is then placed in a cold box for 5 hours at the specified temperature. At the end of which time the previous determined load shall be applied as rapidly as possible while the specimen is still in the cold box, and the deflection recorded 30 seconds later. The calculations are based upon the percentage deflected. The percent change in deflection shall be calculated as follows:

$$C = \frac{D-E}{D} \times 100$$

where C = the percentage change in deflection

D = deflection at room temperature

E = deflection at the temperature of test.

This test is run according to Suffix I which is -40°F and Suffix F2 which is -67°F.

FABRIC STAINING AND DISCOLORATION - Urethane foams will for the most part turn a dark yellow when exposed to direct sunlight. To guarantee or to assure that this discoloration does not stain or discolor the fabric, a standard automotive test has been specified by many of the automobile companies. The sample of foam is wrapped around white vinyl trim and it is exposed for

72 hours under an S-1 sunlamp. The foam is then unwrapped from the vinyl and the white vinyl shall show no darkening, staining or deterioration. Unless the foam should have some large quantities of plasticizer or other type materials in it, I have known of no cases where a general purpose urethane foam failed this particular specification. Another automotive test measures the resistance of foam to solvents and detergents. The test calls for the foam to be immersed in a solvent or detergent solution for 3 hours. The sample is then squeezed dry and there should be no evidence of tackiness and no visual degradation. The type of solvent is usually specified and for the most part corresponds to one of the standard dry cleaning solutions.

HEAT DEGRADATION - Prior in this discussion we elaborated on the heat aging test at 284°F, a second test called heat degradation is also used in the automotive industry. The sample is usually exposed for 336 hours (14 days Ed.) at 212°F. Under these conditions there should be no degradation of the foam.

Unfortunately, I do not know the historical development of this test and cannot indicate why 336 hours was the chosen time period nor 212°F the selected temperature. Yet this is included

in one of the current automotive specifications and I know of no foam that does not pass this test.

OFFENSIVE ODORS - In the development of rigid urethane technology for refrigeration applications, there were many papers issued and many tests run on odor imparting catalysts. The catalyst used in flexible foams also at times can possess some odor. This odor for the most part is of an amine derivative and it does not persist too long in the foam. Yet, to guarantee that this does not degrade the performance qualities of the foam, most specifications include a remark that the foam shall exhibit no odors and usually in parenthesis, offensive odors, wet or dry. They include the word wet, not over concern that the foam may become wet in an open convertible or on lawn furniture, but in the manufacture of some types of bucket seats where it is necessary to stretch the vinyl around the frame structure, steam is used when the pads are slightly oversized to help the vinyl take the drape of the frame and the other padding.

SPECIFIC TESTS FOR FLAME LAMINATING - In the past few years flame laminating has become one of the larger uses of non-seating applications for urethane foams. There is no specific test requirements other than those previously listed to qualify a

foam for flame laminating. The laminator will have specific tests to determine the most critical temperature for the operation, the adjustment of his laminating speeds, pressure on his nip rolls, etc. ASTM and the textile committee has devoted considerable time to the development of test methods for the composite properties and these, of course, would include adhesion, dry cleanability, discoloration, etc. These are all covered in test procedures issued by the ASTM Task Group on Foam-Fabric Laminates, October 16, 1962, Subcommittee A7.

FLAME RESISTANCE - Several methods are used to determine the flame resistance of cellular materials. In latex foam specifications, the flame test is left to the discretion of the purchaser and the exact test is specified between the purchaser and the supplier. Vinyl foams like flexible urethane foams are tested according to ASTM D-1692-59T, "Method of Test for Flammability of Plastic Foams and Sheeting." In this test the specimen of foam measuring 6 inches by 2 inches by 1/2 inch is ignited at one end and the time necessary for the flame to become self-extinguishing is measured. New York State has a similar test in which the specimen is held horizontally and ignited on one end. If the flame does not propagate and is self-extinguishing, the

foam then is washed in hot detergent water and dried and retested. This is to assure that the flame retarding additive is not soluble in ordinary water. Another method used is simply referred to as a cigarette test. In this test the foam can be laid flat or can be folded. In the flat test, a cigarette is lit and laid on the top surface of the foam and the specifications state that the evidence of ignition or burning shall not be greater than 1/4" around the dimensions of the cigarette. A non-flame retardant flexible foam will not normally support combustion in this manner. Latex foams of the general purpose type will usually become ignited, smolder and be completely consumed. In the folded test, it simulates the joining of a cushion with the back of a davenport or a chair. The foam is usually bent back upon itself, a lighted cigarette is placed in the crevice and allowed to burn. Under this test which is specified in the City of Los Angeles Specification Fire Marshall Codes, the foam shall show no ignition properties and no burning. Most of these tests, of course, are superficial in that they are run directly on the foam itself and there are very few applications, except for headliners for automobiles, which will use a flexible foam exposed. Most applications require some

type of ticking or covering of the materials and in this particular case, these tests do not appear to be applicable. A detailed discussion on the flame-resistant properties of foams is the subject matter of another lecture and will be covered in complete detail there.

PART II

RIGID CELLULAR PLASTICS

INTRODUCTION

This part of the discussion will cover the basic tests that are used to characterize a rigid cellular plastic. These test methods are applicable to all types of rigid cellular plastics including urethanes, styrene, vinyls, epoxy, phenolic, as well as others, but not including syntactic foams. Syntactic foams are under the jurisdiction of D-20 Sub VI and because of their very high modulus values require special testing techniques.

These methods are used to characterize foam plastics, they are used as control tests, and for the study of the economics of foam application. By adhering to these methods the entire industry can talk the same language and there will be less danger of misunderstanding when the results are interpolated or even extrapolated.

SAMPLE SIZE AND SAMPLING

If there were such a thing as a standard size sample, it would be a cube 12 by 12 by 12 or a free rise panel 24 by 24 by 2 inches. These forms were suggested many times but the industry and

particularly the segment called the user has been slow to accept this idea. In a foamed-in-place operation it is difficult to say where the specimen should be taken except that a large number will show the variability of the item. When the lowest values are to be used as the "best values" the specimen can be taken from the most critical sections of the foam. Properties obtained on a standard cube or panel enables the foam system to be evaluated independently of the handling and molding techniques. Since this is not the way the foam is used, it will be necessary for the supplier and purchaser to come to an agreement as to how the samples are to be prepared and how the specimens are to be taken. The number of specimens tested is specified in ASTM and should be used for specification work.

CONDITIONING

Before the foams are tested they should be conditioned for a sufficient length of time to arrive at reproducible values. Large buns of urethane will require a longer time to reach room temperature than a thin molded section of polystyrene. Unless otherwise specified for specific tests, all foams should be conditioned for at least 24 hours at $23 \pm 1^{\circ}\text{C}$ at $50 \pm 5\%$ relative humidity.

Polystyrene foams expanded by the live steam technique may require a longer time to come to equilibrium.

DENSITY

Density is weight per unit volume and is determined by ASTM D-1622-63, "Standard Method of Test for Apparent Density of Rigid Cellular Plastics." This apparent density is what is generally referred to in industry as core density. It is determined from a specimen of foam that is free from surface skins, densifications, striation lines or other defects. The specimen is of regular shape whose volume can be calculated and not less than 1 cu.in. in volume (Fig. 11). The value is usually measured in cubic inches and its weight in grams. The density is then calculated as:

$$D = \frac{W}{V} \times 3.80$$

where: D = the density in pounds per cubic foot

W = the weight in grams

V = the volume in cubic inches

3.80 = the constant to convert all units to pounds and cubic feet.

For very low density foams it is often times desirable to correct

for the buoyant effect of air as follows:

$$D = \frac{W_s + W_a}{V} \times 3.80$$

where: W_a = weight of displaced air in grams, calculated by multiplying the values of the specimen in cubic inches by the density of air at atmospheric temperature and pressure (the density of air at 23° and 76 cm of pressure = 0.0194 g. per cu. in.).

Part or sectional density is also measured. The volume of small irregular shaped items can be determined by water displacement while large sections are measured in feet and the weight determined directly in pounds. The volume of the mold can also be determined by a water method and this can be used for volume cost figures. The report should include a complete description of the material, including type, source, core or with surface skin and average density.

Density is one of the most important properties since almost all other properties are predicated on it. The strength properties can be varied over a wide range by only changing the density, density also has an effect on K-factor, MVT and dimensional stability.

The core density is a relatively uniform density of the interior portion of a foam and does not include any skin. It is the lowest density measured on the part or item. The overall density is significant for ascertaining overall weight and cost. It includes all materials that go into the item.

The use of core density as a means of characterizing a foam has several advantages and several disadvantages.

- a) It is the only way of characterizing the effect of polyol variations (urethanes).
- b) It is one way of measuring the efficiency of certain catalysis or copolymer structures (rigid vinyl).
- c) It is a measure of uniformity within a large section.

It does not give an overall efficiency, this is where the skin may contribute to strength properties. The part must be cut to obtain core density values. It cannot be used for volume cost figures. It may yield idealized values that have no relation to performance.

COMPRESSIVE STRENGTH

The compressive strength is the maximum compressive stress which a material is capable of sustaining. Compressive strength is

calculated from the maximum load based on the original cross sectional area of the specimen. The compressive strength is determined according to "Standard Method of Test for Compressive Strength of Rigid Cellular Plastics", ASTM D-1621-64. This method provides information regarding the behavior of cellular materials under compressive load. Procedure A uses the crosshead movement of the testing machine for determining compressive properties and Procedure B employs strain measuring devices mounted on the specimen. Deformation data can be obtained from the load deflection curve. You can calculate the compressive stress at any load and the effective modulus of elasticity.

The test specimen shall be a minimum of 4 sq.in. and a maximum of 36 sq.in. The minimum height shall be 1 inch and the maximum shall be no greater than the width or diameter. Needless to say the loaded ends should be parallel and the sides perpendicular. For reference purposes a minimum of 5 specimens shall be tested. Since most foams are anisotropic, duplicate sets are tested having the compression axis parallel and normal to the direction of anisotropy.

After the specimens are measured to a precision of ± 1 percent,

the load is applied uniformly over the entire loading surface of the specimen. The rate of loading shall be 0.01 in. per minute per inch of thickness. For Procedure A set the crosshead travel to give 10% deformation of the measured thickness. For Procedure B compress the specimen to a strain of 2 percent.

The compressive strength is calculated by dividing the maximum load in pounds by the area of the specimen in square inches. If no maximum load exists before 10 percent deformation based on crosshead movement, or 2 percent strain, record the maximum load at 10% deformation or 2% strain.

ASTM C-165-54, "Method of Test for Compressive Strength of pre-formed Block Type Insulation", is also used to measure the compressive strength of rigid cellular plastics. The specimen size is 6 by 6 by 1 inch. The specimen is dried 16 hours in a vented oven at a selected temperature between 215 and 250°F. The rate of loading shall be 0.05 in. per min., and the deformation at 5% is recorded.

Figure 12 shows a stress-strain curve for a 2 pound density foam. This curve does not conform to Hooke's Law (stress proportional to strain) throughout its elastic range, it has become the standard

practice to calculate only the tangent modulus. The tangent has a slope following the greatest portion of the loading curves that is essentially a straight line. Since the stress-strain curve is slightly "S" shaped, the actual tangent modulus drawn to the longest straight line portion of the curve is a realistic estimate of the stiffness of the foam.

The compressive strength determination can also be run at elevated temperatures. The procedure is identical to the room temperature test with the addition of a conditioning time for the foam. A right cylinder 1.13 in. in diameter by 1 in. in thickness has been used and conditioning of 30 minutes at each temperature recommended. A larger specimen will require a longer time to come to equilibrium.

Because of the shape factor the small size specimen will yield lower results than the minimum 4 sq.in. recognized in D-1621. Needless to say C-165 and D-1621 do not give identical values.

TENSILE STRENGTH AND MODULUS

The tensile properties of rigid cellular plastics are determined according to D-1623-64. This method is used for determining the

tensile properties of test specimens of standard shapes under given conditions of temperature, humidity and testing machine speed. Two types of tensile specimens are recognized. Type A is dog bone in shape and prepared on a lathe, while Type B is a flat specimen having a minimum area of 1 sq.in. and bonded to suitable fixture, Figures 13, 14 and 15.

A minimum of five specimens shall be tested. They shall be conditioned and tested at $23 \pm 1^{\circ}\text{C}$ and 50% R.H. The suggested rate of loading should be 0.05 in. per minute of test section gage or such that the rupture occurs in from 3 to 6 minutes.

TYPE A - The foam specimen 6 by 2 by 2 is shaped on a lathe, rotating at a high speed, using a special cutter to a 1.129 inch diameter restricted portion to fit into the specimen holder. If the foam is soft and has a tendency to crush under loading the ends may be dipped into a low melting point wax. This method is accurate and reproducible but requires a relatively large sample of foam. It cannot be used on thin panels, or completely molded shapes.

TYPE B - The foam is cut from any defect-free specimen, it shall be round or square, having a minimum cross-sectional area of

1 sq.in. The specimen is bonded to the grips with a suitable adhesive. Bondmaster M666* has been found adequate for this application. M666 is a two-component epoxy, solvent-free, having the consistency of honey. It usually takes 24 hours to reach maximum cure.

The small specimen size introduces possible error caused by minor variations in the foam. Specimens of 4 sq.in. are often used and this larger size helps to increase the reproducibility.

Elongation measurements can be made directly using the Type B specimen while gage marks or an extensometer must be mounted on Type A specimens.

Since foams are seldom used in tension, the tensile test has limited value. Type B does have many uses. It is identical to C-297-61, the "Tension Test of Flat Sandwich Construction in Flatwise Plane". This is used to determine the adhesion properties of foam laminates and is also useful in determining the interply adhesion of spray foams or foams that have adhesion layers resulting from multipours.

* Manufactured by Pittsburgh Plate Glass Company.

FLEXURAL STRENGTH

The flexural strength of rigid foam is determined by ASTM D-790, "Standard Method of Test for Flexural Properties of Plastics".

This sophisticated test was not written specifically for foams, but for solid plastic and electrical insulating materials. A bar of rectangular cross-section is tested in flexure as a simple beam. The load is applied in the center of the specimen midway between the supports. The loading nose and supports shall have cylindrical surfaces. To prevent excessive indentation, the radius of the nose and supports shall be at least 1-1/2 times the specimen depth.

The recommended specimen size is 6 by 1/2 by 1/4 inch. They should be free of voids, skin or any visual defects. The rate of loading should be 0.1 inch per minute and a span of 4 inches.

Calculations of Flexural Strength and Modulus

$$S = \frac{3 PL}{2 b d^2}$$

where: S = stress in outer fiber at midspan in psi.

P = load at a given point on the load deflection curve.

L = span in inches.

b = width of the beam, and

d = depth of the beam.

Flexural Modulus

$$E = \frac{L^3 M}{4 b d^3}$$

where: E_B = modulus of elasticity in bending, psi.

L = span in inches

b = width in inches

d = depth in inches, and

m = slope of the tangent to the initial straight-line portion of the load deflection curve in pounds per inch of deflection.

The flexural strength test is also run at low and elevated temperatures because it gives useful information for possible end use applications. Testing jigs are easy to make and very little additional equipment is needed. Like all tests with small-sized specimen reproducibility is drastically affected by imperfections such as voids, cracks, blisters and striations.

For composite structures with rigid skins and foam core, ASTM C-393-62 is recommended, "Tentative Method of Flexure Test of Flat Sandwich Constructions." This test consists of loading a specimen at quarter points to produce curvature of the plane of a sheet of sandwich construction. This test is

conducted to determine flexural and shear stiffness of the construction, shear modulus and shear strength of the core, or compressive or tensile strength of the facing. A recommended specimen size is 19 by 3.5 inches by thickness. A span of 16 inches and a rate of loading such that the failure occurs in 3 to 6 minutes. This is a very interesting test and is applicable to all types of sandwich construction.

The British method is similar to D-790, except it only specifies the specimen size, the span and rate of loading. No calculations are required, the load is reported as read from the testing machine. This simple treatment of the flexural properties may be all the subject really deserves since it is more a property type of test rather than a performance test.

SIMULATED SERVICE CONDITIONS

Environmental testing is done according to ASTM D-2126-67, "Method of Test for Resistance of Rigid Cellular Plastics to Simulated Service Conditions." This method provides a number of conditions for the artificial aging of rigid cellular plastics. The test consists of exposing the specimens at various conditions and determining a change in weight, volume

or linear dimensions. The specimen size is 4 by 4 by 1 inch and is sawed from the sample so as to have smooth edges and be free of defects and dust. Seven conditions are listed:

Procedure A - $23 \pm 1^{\circ}\text{C}$ and 50% R.H.

B - $-29 \pm 3^{\circ}\text{C}$

C - $38 \pm 1^{\circ}\text{C}$ and 90 to 100% R.H.

D - $60 \pm 1^{\circ}\text{C}$ and 90 to 100% R.H.

E - $70 \pm 1^{\circ}\text{C}$

F - $70 \pm 1^{\circ}\text{C}$ and 90 to 100% R.H.

G - $100 \pm 1^{\circ}\text{C}$.

When the revision of this method is completed this year it will include additional temperatures and humidities to broaden the usefulness of the test.

This method does not require intermediate measurement between the initial and 28 day reading, yet it is a routine practice in most laboratories to make measurements at the end of 1, 2, 7, 14 and 28 days. Since the cell in urethane foams is egg shaped the dimension of the specimen does not expand or contract uniformly. At 70°C and 90 to 100% R.H. the dimension measured along the axis of the cell may decrease, while the other two dimensions will increase. It is not uncommon to find reversal

and collapse after 14 days exposure. Moisture apparently softens the plastic and the closed cells expand and break the windows and the structure breaks down. Environmental aging of other types of cellular plastics does not appear to constitute a serious problem. In the evaluation of urethane foams this test is the most time consuming and most difficult to interpret because foam is seldom used in the exposed state, but usually has some type of protective skin or coating.

ANALYTICAL METHODS

The chemical analysis of urethane foam raw materials are covered in detail in ASTM D-1638-67. This method covers procedures for testing raw materials used in preparing urethane foams. The raw materials covered are toluene diisocyanate and polyols, including both polyesters and polyethers. For TDI the tests included are:

Sampling	Assay
Isomer Content	Total Chlorine
Hydrolyzable Chlorine	Acidity
Freezing Point	Specific Gravity
Color.	

For polyols the tests included are:

Sampling	Sodium and Potassium
Acid and Alkalinity Numbers	Hydroxyl Number
Unsaturation	Water
Suspended Matter	Specific Gravity
Viscosity	Color
Total Basicity.	

This document is under current study by the SPI and ASTM and will be expanded to include polymeric isocyanates and polyols other than the ones now covered. Raw materials for other rigid foams are usually in-house tests and there has been no recent request to have these published as standards. This work is under the jurisdiction of D-20 Sub 20.

FRIABILITY AND CRUSHING RESISTANCE

Friability, crushing, brittleness and abrasion resistance are all grouped together because they are similar properties.

There are no official methods used to measure these properties.

Some of the CO₂ blown urethanes are very friable to the touch, so several methods were lifted out of other procedures and used.

They included ASTM C-421-61, "Method of Test for Weight Loss

by Tumbling of Preformed Insulation", and C-376-57, "Method of Test for Strength Properties of Prefabricated Architectural Accoustical Materials." (Fig. 16). Both tests consisted of tumbling small cubes of foam with cubes of red oak in a wooden box for 2 and 8 minutes. The weight loss of the foam serves as a relative measure of friability and abrasion resistance. Using this method it is necessary to delete the requirement for drying the specimen for 20 to 24 hours at 215 to 250°F. Polystyrene foams exhibit a nil loss while the urea-formaldehyde foams may turn into a powder. Static charges on the urethane would often adhere them to the box and they would not tumble at all. Abrasion resistance of high density foam has been measured by the National Bureau of Standards abraider. The number of cycles to wear through 0.10 inch of foam was reported. To determine surface brittleness an educated thumb or finger are often employed. The surface brittleness may be a transient property and upon heat curing or simply with time will disappear. An instrument originally developed to measure the penetration force required to rupture a hot dog skin is being studied to measure surface brittleness. (Fig. 17). Panels or other pour-in-place items must not be moved roughly until this

surface brittleness disappears or there will be no bonding between the skins and the panel.

The Taber abraser is under study to determine if this apparatus can be used to measure friability (Fig. 16). Specimens 4 by 4 by 0.25 inch are cut from a homogeneous sample. The thickness is measured to the nearest 0.001 inch. The H-18 (carborundum) wheels without additional weights on the arms are used to abraid the foam. A wheel made with 100 mesh stainless steel screen is under study. The foam dust does not clog the surface as with a stone wheel. The number of cycles required for the wheels to wear through are determined. The value is then calculated for a 1 inch thick sample. The results obtained by this method corresponded with the results of an educated thumb while other methods such as an analysis of a compression deflection curve may prove inconclusive. For urethane foams the Taber method appears to correspond fairly well with C-421. This method has yet to be tried on vinyl, epoxy or phenolic foams. This proposed method is easy to run and eliminates the weighing operation.

FLAMMABILITY TESTING

The flammability testing of cellular plastics deserves more attention than being treated as a part of this discussion and will be covered in detail by another speaker.

WATER ABSORPTION

ASTM D-2127-62T, "Tentative Method of Test for Water Absorption of Rigid Cellular Plastics," consists of determining the absorption of water by rigid cellular plastics when immersed under a 2-in. head of water. The amount of water absorbed will change with immersion time and it is impracticable to carry the exposure to equilibrium. An intermediate period such as 24 hours allows comparisons with previous results.

A specimen 4 by 4 by 1 inch is sawed from a uniform sample of foam. Three specimens constitute the test. The specimen is weighed and the dimensions measured. It is then placed under a 2-inch head of water for approximately 10 seconds, the specimen is removed and allowed to drain for 10 seconds at an angle of 30 degrees from the vertical on a 1/4 inch mesh screen. The specimen is weighed to get the zero absorption value. The specimen is then immersed for 24 hours under a 2-inch head of water and the final weighing is done using the 10 second drain

time. Calculations: The amount of water absorbed can be calculated several ways:

- a) A percent increase in weight.
- b) Pounds of water absorbed per cubic foot.
- c) Pounds of water absorbed per square foot.
- d) Grams of water absorbed per 1000 sq. cm.
- e) Grams of water absorbed per 1000 cu. cm.

Calculations "d" and "e" are specified in ASTM.

This method has been under continuous study for five years. Several modifications have been tried and these include: adding a small amount of detergent to the room temperature water; blotting dry the specimen with a towel; wiping off the excess water; dipping in alcohol and drying in an air current with a fan; using a 10 ft. head of water and lastly development of a new test based on measuring the buoyancy of the foam. The alcohol method may work well with urethane foams, but may cause trouble with other types of foams. The test method should be applicable to all types to be valid as a comparison test for cellular materials. Long term immersion, one to two years, yields many interesting results, some foams absorb water immediately and can be used for floral decorations,

polystyrene foams will remain virtually unchanged while some urethanes may become transparent and completely water logged.

POROSITY

The porosity of cellular foams can be measured by two methods: ASTM-D-1940, "The Glassware Apparatus" and the Beckman Pycnometer (Fig. 18). The Beckman Pycnometer method will be voted on this year by D-20. The glassware apparatus is based on volumetric displacement of air by the specimen at constant pressure while the pycnometer measures the volumetric displacement of the specimen under a pressure differential. Regardless of the method used, sample preparation is very critical. The foam should be cut with a sharp cutting tool that does not tear or rip the foam specimen. A power driven cork borer has been used with some success.

Once the volume is determined, the specimen can be cut again, increasing the surface to volume ratio and exposing more open cells. The specimens are remeasured and it is possible to calculate % closed cells, % open cells and % cell walls.

Calculations: Calculate the true volume V_1 of each specimen from its individual measurements of height and diameter.

If measurements are made in inches, convert to cu.cm.

$$V_1 = 12.870 d_1^2 h_1$$

% Open Cells

$$O_c = \frac{V_1 - \Delta V_1}{V_1} \times 100$$

where: ΔV_1 is the volume obtained from the instrument.

% Cell Wall

$$C_w = \frac{D_f}{D_s} \times 100$$

where D_f = density of the foam

D_s = density of the solid polymer

% Closed Cells

$$C_c = 100 - O_c - C_w$$

The correction for cells opened by cutting is covered in detail in the ASTM documents. The two methods have been shown to agree quite closely. An excellent paper on porosity measurement was given by Remington and Pariser and also by Harding. The apparatus specified in several of the military specifications is similar in operation to the glass apparatus.

WATER VAPOR TRANSMISSION

Water vapor transmission is measured according to ASTM C-355, "Water Vapor Transmission of Material Used in Building Construction." The rate of water vapor transmission, WVT is the

time rate of water vapor flow between two specified parallel surfaces under study conditions through a unit area, under the test conditions. An acceptable unit of WVT is 1 grain per hour square feet. Water vapor permeance is the ratio of its WVT to the vapor pressure difference between the two surfaces. The accepted unit is the perm., or 1 grain per sq. ft. hr. inch of mercury. Water vapor permeability is the product of its permeance and thickness. The accepted unit of permeability is perm inch or 1 grain per sq. ft. hr., in. of mercury per in. of thickness. Since foams are homogeneous throughout their thickness, permeance is indirectly proportional to thickness.

This method covers two procedures, the dry cup and wet cup technique. In the desiccant or dry cup method the specimen is sealed to the open mouth of a test cup containing a desiccant and the test assembly is placed in the specified atmosphere. Periodic weighings determine the rate of water vapor movement. In the Water Method the desiccant is replaced with pure water and the weighings determine the rate of water vapor through the specimen.

The results of the two methods are not comparable, with the desiccant method giving lower values. A wax seal composed of

a 50-50 beeswax and rosin is used to seal the foam in the cup. As long as the test conditions are mild the seal does not break. If the test conditions are 100°F at 95 to 100% R.H., the wax will usually crack upon cooling and resealing will be necessary.

The test cup is usually weighed each day for 7 to 10 days and the weight plotted against elapse of time. The curve will tend to become a straight line after three or four days. Judgement here is required and numerous points are helpful.

Calculations -- Water Vapor Transmission

$$WVT = \frac{G}{tA} = \frac{G/t}{A}$$

where: G = weight change in grams from straight line

t = time in hours during which G occurs

G/t = slope of the straight line in grams per hour

A = test area in square feet

WVT = grains per sq. ft. hr.

$$\text{Permeance} = \frac{WVT}{p} = \frac{WVT}{S(R_1 - R_2)}$$

where: p = vapor pressure difference in inches of mercury

S = saturation vapor pressure at test temperatures,
in inches of mercury

R₁ = relative humidity at the source, and

R₂ = relative humidity at the sink.

An alternate method is now being studied, it is quicker and not quite as precise. It is called the rubber sleeve method. A specimen 4 in. in diameter is cut from a one inch thick slab. It should be free of surface skin, voids, cracks or other defects. The top of a Size 9 latex glove is stretched over a desiccant filled 100 x 50 mm. Pyrex dish and over the edge of the foam. Round robin studies so far have indicated that this method is reproducible but yields higher values than the C-355 method.

THERMAL COEFFICIENT OF EXPANSION

A dilatometer is used to measure the thermal coefficient of expansion according to ASTM D-696-44. This method was not written for cellular plastics and may yield erroneous results. This method is intended for determining the reversible linear thermal expansion through a temperature range of -30°C to $+30^{\circ}\text{C}$. The values obtained by this method gives only approximate values.

HEAT DISTORTION TESTS

There are many types of heat distortion tests, yet none have received official recognition. A subcommittee of D-20 is actively working on several methods in an attempt to establish a standard. Some are quite simple while others require elaborate

equipment. A brief description of the many methods under consideration will give you some idea of how involved this type of work can be.

METHOD NO. 1- Volume change at 250°F.

Scope - This method consists of subjecting a sample of foam for 4 hours at 250°F and determining the volume change.

Condition - Temperature -250°F

Sample size - 2" x 2" x 2" or 4" x 4" x 1"

Duration - 4 hours

Procedure - 1. Determine the original volume.

2. Expose the sample for 4 hours at 250°F

3. Remove the sample and allow it to come to equilibrium for 1/2 hour in the CTH room.

4. Determine the final volume

5. Calculate the percent volume change.

Remarks - The volume change after only 4 hours appears to give incomplete data and is not an indication of long term performance. It is often advisable to extend the time to 28 days and interesting data is obtained.

<u>Days</u>	<u>% Volume Change</u>
4 hrs.	4
1 day	7

<u>Days</u>	<u>% Volume Change</u>
2 days	10
7 days	18
14 days	22
28 days	30

For each polyol system and every density there will be a separate set of data.

METHOD NO. 2 - Compression Set

Scope - This method consists of subjecting the foam to a static load of 5 psi. at 70°C for 24 hours.

Condition - Temperature - 70°C (158°F)

Sample size - cylinder 1.129 diameter by 1 inch high

Duration - 24 hours

Compression set jig

- Procedure - 1. With a hole saw, cut a cylinder of foam that has a diameter of 1.129" and a height of 1 inch.
2. Place the specimen in the jig and apply the 5 pound load.
 3. Place the unit in the oven at 70°C for 24 hours
 4. Remove the specimen and allow it to come to equilibrium in the CTH room for 1 hour. Determine the final height.
 5. Calculate the percent change in height.

Remarks - This test method has been used for several years in government speculations. The 5 pound static load is only 1/6 of the yield point of a 2 pcf. foam. The temperature is very low when you consider some of the published data for maximum performance temperatures.

A foam can be deflected by this method and then during the one hour waiting period recover. This test method assumes that the softening effect of temperatures is linear and that 5 pounds will measure the mixed effect of static loading, creep, and stress relaxation.

METHOD NO. 3 - K-Factor Retention

Scope - This test consists of measuring the effect of moderate heat aging on K-factor retention.

Condition - Temperature - 60°C (140°F)

Sample size - 6" x 6" x 1/2"

Duration - 10 days

Apparatus - Guarded hot plate

Procedure - 1. Determine the original K-factor.

2. Expose the same specimen for 10 days at 60°C.

3. Determine the final K-factor.

4. Calculate the percent retention.

Remarks - There has been a lot of published data to show that the K-factor will increase as other gases and vapors permeate

the foam. When the foam is exposed at 60°C for 10 days, the rate of gas convection is increased; and, hence, the insulating value of the foam decreases. The polyol backbone, the type of NCO material, the index and density all effect K-factor retention. Why was 60°C selected as the test temperature, why not 70 or 80 or even 100°C? Over 4 years ago, uncut samples of rigid foam measuring 0.5 cu. ft. were placed in the 60° oven. The foams had paper on 5 of the 6 surfaces. Some were under indexed, some were over indexed, and foams at 105 indices were used as control. None of the foams, regardless of index, varied more than 5.2% from the original. It may be inferred that these foams were of exceptional quality or, 60°C is not severe enough to determine K-factor drift.

METHOD NO. 4 - Low Load Heat Distortion Test

Scope - This method consists of subjecting a specimen of rigid foam to a static load of 100 grams per sq. inch and measuring the percent set.

Condition - Temperature - any desired temperature

Sample size - 3" x 3" x 1"

Duration - 24 hours

Apparatus - Compression set jig with a 1 sq. inch indenter presser foot.

Procedure - 1. Measure the thickness to the nearest 0.001 inch.

2. Place the foam in the test jig and apply the 100 gm. load on the presser foot of 1 sq. inc.
3. Place the apparatus in the oven at the selected temperature for 24 hours.
4. Remove the apparatus from the oven and immediately place the foam specimen in the CTH room for 1 hour.
5. Determine the final height and calculate the percent change of the released specimen.

Remarks - The weight of 100 grams constitutes a load of only 0.22 psi. This is only a small fraction of the normal room temperature compressive strength, so it is reasonable to assume the extremely higher temperatures will be needed to obtain any sizable deflection. At moderate temperatures the foam expands and actually overcomes the force of the load. In this case, the percent change will be positive.

METHOD NO. 5 - Temperature at which 5% Volume Change Occurs

Scope - This method covers the procedure for determining the temperature at which the foam expands 5 percent by volume.

Condition - Temperature - Any oven capable of being set at 10°C increments and with a maximum setting of 250°C.

Sample size - 2" x 2" x 2"

Duration - 1 hour

Procedure - 1. Accurately determine the volume of a 2 x 2 x 2 inch cube of foam.

2. Set the oven at 120°C.
3. Expose the sample for 1 hour.
4. Remove the sample and allow it to come to equilibrium in the CTH room for 1 hour. Immediately after removing the specimen, set the oven at 130°F.
5. Determine the second volume and calculate the volume change. If the change is less than 5%, replace the specimen in the oven for 1 hour at 130°C.
6. Repeat this procedure until the volume change is 5% or greater.
7. Record the previous temperature as the heat distortion temperature.

Remarks - This test method is time consuming and there is the problem of relating this value to use data.

METHOD NO. 6 - Heat Softening Temperature

Scope - This method covers a procedure for determining the temperature at which a foam softens and is unable to support a load of 100 grams.

Conditions - Temperature - An oven capable of increasing temperatures from 20 to 250°C at a uniform rate in one hour.

Sample size - 6" x 1" x 1"

Testing jig - 4 inch span, 100 gm. loading at mid point.

Procedure - 1. Place the testing jig in the oven with the rod indicator protruding from the top of the oven.

2. Place the specimen in the jig and apply the 100 gm. load at the mid point on the 3/16 dia. by 1" loading nose.

3. Turn on the oven to maximum temperature.

4. Record the temperature at which the sample fails.

Remarks - This method is very good when you are studying the effect of polyol structure. It has also been used to show the difference between polyols with varying amounts of diol.

Density has a significant effect on this heat distortion temperature. This constitutes no major difficulty since a series of densities can usually be made. The rate of temperature rise is critical and must be taken into consideration for standardizing the test method.

METHOD NO. 7 - Heat Distortion Time at 200°C

Scope - This method describes the procedure for determining the time to failure when the foam is tested at 200°C

and with a mid point loading of 100 grams.

Conditions - Temperature - 200°C

Sample size - 6" x 1" x 1"

Testing jig - Foam is tested as a simple beam with a span of 4" and a mid point load of 100 grams.

Procedure - 1. Place the test jig in the oven.

2. Set the oven at 200°C.
3. Turn off the fan, open the oven and place the specimen in the jig, apply the load, close the door and turn on fan, and immediately start the time.
4. At the end of one minute, the oven should be back at 200°C and note the position of the measuring rod.
5. Take reading every 1 minute until failure or to a total time of 15 minutes, whichever occurs first.

Remarks - This test method has proven to be very useful in determining the effect of polyol, NCO and catalyst on foam properties. When the deflection is plotted versus time, it is possible to determine the heat softening and distortion point. The load of 0.22 pounds equals a static distortion maximum fiber stress of 2.64 psi. This is about 18% of the force required to break the specimen at room temperature.

METHOD NO. 8 - Physical Properties at Elevated Temperatures

Scope- This method covers the procedure for determining the compressive strength and flexural strength at elevated temperatures.

Conditions - Temperature - Any temperature up to 700°F.

Sample size - 2" x 2" x 2" or 1.129 diameter x 1" height.

Apparatus - Instron with environmental cabinet.

- Procedure - 1. Position the environmental cabinet in the Floor Model Instron. Attach the compressive cage for compression deflection or the flexural jig for flexural strengths.
2. Use the test procedure as for room temperature testing. See ASTM D 1621-59T for CD or ASTM 790-61 Method A for flexural strength.
3. Set the thermostat to the desired temperature.
4. Determine the compressive strength or flexural strength.

Remarks - This test method is time consuming, and yet is very worth-while. All rigid urethane foams soften with an increase in temperature and have lower compressive strength properties.

The percent retention at a given temperature depends on the many

chemical and physical parameters.

<u>Sample</u>				<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>
R.T. Flexural strength, psi.				63.2	63.6	58.1	96.6	64.8	57.4
100°C	"	"	"	18.7	46.7	38.8	0	46.7	32.9
150°C	"	"	"	7.1	6.6	19.0	0	0	0

Sample D was polystyrene

Sample C at 150°C had 39% retention of properties.

Other methods considered were the Clash-Berg Torsional modulus and shear strength.

SHEAR TEST

Shear strength is measured according to ASTM C-273-61, "Method of Shear Test in Flatwise Plane or Flat Sandwich Constructions or Sandwich Core" Shear strength is the maximum shear stress a material is capable of sustaining. Shear strength is calculated from the maximum load and is based on the original cross sectional area of the specimen. From the complete load-deformation curve it is possible to compute shear stress of the sandwich or core at any load and to compute an effective shear modulus of the sandwich as a unit or shear modulus of the core. This test does not produce pure shear, but the specimen length is prescribed so that secondary stresses have a minimum effect.

The test specimen should have a thickness equal to the thickness of the sandwich, a width not less than twice the thickness, and a length not less than 12 times the thickness.

For routine work a sample size of 6 by 2 by 0.5 in. is commonly used. It is adhered to the testing jig with a suitable adhesive such as two-component epoxy. The testing plates of the jig should have a stiffness of not less than 600,000-lb.-in.² per inch of width per inch of core thickness. The load is applied in compression or tension at a rate that the maximum load will occur within 3 to 6 minutes. The suggested rate of loading is therefore 0.005 in. per in. of specimen length. The deformation is read to the nearest 0.0001 in. by means of an optical lever system, dial gage or other suitable means.

Calculations: Shear Stress = $f_s = \frac{P}{Lb}$

where: f_s = shear stress in pounds per square inch

P = load on the specimen in pounds

L = length of specimen in inches

b = width of the specimen in inches.

Shear Strain = $\gamma = \frac{r}{t}$

where: r = dial reading or movement of the face plate

of test jig with respect to the other, in inches

t = distance between the plates.

It should be noted that the effective shear modulus obtained by this method is that of a combination of all the materials between the face plates acting as a unit. The theoretical relationship of this modulus, G , to the modulus of the facing, G_f , and of the core, G_c , is expressed as follows:

$$\frac{1}{G} = \frac{h - c}{G_f h} + \frac{c}{G_c h}$$

where the respective moduli are those associated with shearing strains in a plane normal to the facing and parallel to the direction of applied forces.

h = total thickness of sandwich in inches, and

c = thickness of core, in inches.

If failure occurs in the bond between the loading plates and the specimen, the test shall be considered unsatisfactory unless the specimen shows severe shear distortion and partial shear failure before final failure. Shear strength is of greatest importance to the building industry and for reliable results it is necessary to comply exactly with the method.

THERMAL CONDUCTIVITY

The thermal conductivity, k , of a homogeneous material is the time

rate of heat flow, under steady-state conditions, through unit area, per unit temperature gradient in the direction perpendicular to an isothermal surface. For a flat slab of foam it is calculated as follows:

$$k = \frac{qL}{A(t_1 - t_2)}$$

where: k = thermal conductivity in Btu in. per hr. sq. ft.
deg. Fahr.

q = time rate of heat flow, in Btu per hr.,

L = thickness of specimen measured along a path normal to isothermal surfaces, in inches,

A = area in sq. ft.,

t_1 = temperature of hot surface, in deg. Fahr., and

t_2 = temperature of cold surface, in deg. Fahr.

The value " q " is usually measured in watts and then converted to Btu's. The construction of the electric heating plate has been discussed by several investigators and this is a subject in itself.

The thermal conductivity of a foam may vary due to variability of the foam, it may be affected by moisture or other conditions, and may change with time or high temperatures.

There are several methods for measuring thermal conductivity.

ASTM C-177 -- "Test for Thermal Conductivity by Guarded Hot Plate."

C-518-63T -- "Thermal Conductivity of Materials by Means of a Heat Flow Meter."

D-2326-64T -- "Thermal Conductivity of Cellular Plastics by Means of a Probe."

The guarded hot plate is the industry standard and is used where accurate and absolute values are required. This method is not valid for temperatures lower than -100°F . The thermal probe is a fairly simple piece of equipment and k-factor values can be made in a short time after a fairly long condition period. For precise work the temperatures must be held and measured to $\pm 0.1^{\circ}\text{C}$. Some error will be introduced with high density foam (over 4 pcf.) because of the high heat capacity of the foam since this method depends on measuring the heat rise. The probe is used extensively with froth foam because of the difficulty of obtaining uniform specimens as required for the guarded hot plate method.

The heat flow meter is a secondary method for measuring thermal conductivity because its calibration depends on a primary standard which has been accurately determined by a guarded hot plate.

A modified guarded hot plate method has found wide acceptance with manufacturers of rigid cellular plastics. The modified guarded hot plate gives results very close to those obtained by a guarded hot plate at a mean temperature of 75°F. Like the heat flow meter the equipment must be standardized with a reference sample determined by the guarded hot plate. These are available from the National Bureau of Standards in Washington. A k-factor can be determined in 20 to 30 minutes with a precision of ± 0.005 using a relatively small specimen (2 pieces 6 by 6 by 0.5 in.).

There are many other tests used to evaluate rigid foams and they will not be discussed in detail. They include electrical properties, sound properties, creep, solvent resistance, specific heat, thermal diffusivity, processability, bead bond knit, void and cell measurements, foam initiation time, rate-of-rise, time, and the whole host of special tests which are too numerous to discuss. Included in the appendix is a list of standard tests used in the evaluation of cellular plastics.

ACKNOWLEDGEMENT

The author wishes to express his appreciation to Dr. John T. Patton, Jr., and S. Davis for their assistance in reviewing this paper.

APPENDIX

SUMMARY OF ASTM TEST METHODS & SPECIFICATIONS

APPROVED FOR CELLULAR PLASTICS

<u>ASTM Designation</u>	<u>ASTM Committee</u>	<u>Title</u>
<u>ASTM Physical Test Methods for Rigid Cellular Plastics</u>		
C-177-45	C-16	Method of Test for Thermal Conductivity of Materials by Means of the Guarded Hot Plate
C-203-58	C-16	Test for Breaking Strength of Preformed Block-Type Thermal Insulation
C-273-61	C-19 ^o	Method of Shear Test in Flatwise Plane or Flat Sandwich Constructions or Sandwich Cores
C-355-63T	C-16	Tentative Methods of Test for Water Vapor Transmission of Materials Used in Building Construction
C-393-62	C-19	Tentative Method of Flexure Test of Flat Sandwich Constructions
C-518-63T	C-16	Tentative Method of Test for Thermal Conductivity of Materials by Means of a Heat Flow Meter
D-149-61	D-9	Test for Dielectric Breakdown Voltage & Dielectric Strength of Electrical Insulating Materials at Commercial Power Frequencies

<u>ASTM Designation</u>	<u>ASTM Committee</u>	<u>Title</u>
D-257-61	D-9	Test for Electrical Resistance of Insulating Materials
D-790-61 (Method A)	D-20	Method of Test for Flexural Properties of Plastics
D-1621-64	D-20	Method of Test for Compressive Strength of Rigid Cellular Plastics
D-1622-63	D-20	Method of Test for Apparent Density of Rigid Cellular Plastics
D-1623-64	D-20	Method of Test for Tensile Properties of Rigid Cellular Plastics
D-1673-61	D-9	Method of Test for Dielectric Constant & Dissipation Factor of Expanded Cellular Plastics Used for Electrical Insulation
D-1692-59T	D-20	Tentative Method of Test for Flammability of Plastics Foams and Sheeting
D-1940-62T	D-20	Tentative Method of Test for Porosity of Rigid Cellular Plastics
D-2126-62T	D-20	Tentative Method of Test for Resistance of Rigid Cellular Plastics to Simulated Service Conditions.
D-2127-62T	D-20	Tentative Method of Test for Water Absorption of Rigid Cellular Plastics

<u>ASTM Designation</u>	<u>ASTM Committee</u>	<u>Title</u>
D-2326-64T	D-20	Thermal Conductivity of Cellular Plastics by Means of a Probe

ASTM Specifications for Rigid Cellular Plastics

D-2125-62T	D-20	Tentative Specification for Cellular Polystyrene
D-2341-65T	D-20	Tentative Specification for Rigid Urethane Foam

ASTM Test Method for Processibility of Cellular Plastics

D-2237-64T	D-20	Tentative Method of Test for Rate-of- Rise Properties of Urethane Foam
------------	------	---

ASTM Test Methods & Specifications for Raw Materials
of Cellular Plastics

D-1638-66	D-20	Methods of Chemical Analysis of Urethane Foam Raw Materials
D-1786-66	D-20	Specifications for Toluene Diisocyanate and Poly(Oxypropylene Glycol)

SUMMARY OF OTHER ASTM METHODS THAT ARE SOMETIMES

USED FOR RIGID CELLULAR PLASTICS

C-165-54	C-16	Method of Test for Compressive Strength of Preformed Block Type Insulation
C-297-61	C-19	Tension Test of Flat Sandwich Construction in Flatwise Plane
C-351-61	C-16	Method of Test for Mean Specific Heat of Thermal Insulation

<u>ASTM Designation</u>	<u>ASTM Committee</u>	<u>Title</u>
C-367-57	C-20	Strength Properties of Prefabricated Architectural Acoustical Materials (Friability)
C-384-58	D-20	Method of Test for Impedence and Absorp- tion of Acoustical Materials by the Tube Method
C-421-61	C-16	Method of Test for Weight Loss by Tumbling of Preformed Insulation
C-585-66T	C-16	Dimensional Standard for Preformed Rigid Thermal Insulation for Pipe & Tubing for Use at Temperatures up to 1200F
C-589-66T	C-16	Apparent Impact Strength of Preformed Block Type Thermal Insulation
C-591-66T	C-16	Tentative Specification for Rigid Pre- formed Cellular Urethane Thermal Insulation (Limited to Temperatures of -100F to 230F)
D-732-46	D-20	Method of Test for Shear Strength of Plastics
D-756-56	D-20	Methods of Test for Resistance of Plastics to Accelerated Service Conditions

<u>ASTM Designation</u>	<u>ASTM Committee</u>	<u>Title</u>
D-757-59	D-20	Method of Test for Flammability of Plastics, Self-Extinguishing Type
D-1924-63	D-20	Rec. Practice for Determining Resistance of Plastic to Fungi
E-96-63T	E-1	Method of Test for Water Vapor Trans- mission of Materials in Sheet Form
E-143-61	E-1	Method of Determining Shear Modulus at Room Temperature
<u>FLEXIBLE FOAMS</u>		
D-1055-62	D-11	Spec. and Methods of Test for Latex Foam
D-1056-65T	D-11	Spec. and Method of Tests for Sponge and Expanded Cellular Rubber Products
D-1564-64T	D-11	Methods of Testing Slab Flexible Urethane Foams
D-1565-66	D-11	Spec. and Methods of Test for Flexible Foams made from Polymer or Copolymer of Vinyl Chloride
D-2406-65T	D-11	Methods of Testing molded Flexible Urethane Foams

British Standards Institution

Technical Committee PLC/RUC/1 Polyurethane Foam

D65/10386 - Testing Rigid Polyurethane Foam

International Organization for Standardization

ISO/TC 61- Plastics

535 -- Compressive Test of Rigid Cellular Materials

537 -- Determination of Apparent Density of Rigid Cellular Materials

633 -- Nomenclature for Cellular Plastics Terms

Military and Government

U. S. Government --

Mil-S-25392 (USAF) 6 Nov. 1957

Sandwich Construction, Plastic Resin, Glass Fabric Base,
Laminated Facings and Polyester-Diisocyanate Foamed-in-Place
Core, for Aircraft Structural Application

Mil-1-14511(Ord) 25 April 1952

Insulation Sheet, Cellular, Plastic, Thermal

Mil-C-8087B (ASG) 9 March 1961

Core Material, Foamed-in-Place, Polyester-Diisocyanate Type

Mil-P-26514 (USAF) 1 May 1959

Polyurethane Foam, Rigid or Plastic, for Packaging

Mil-P-21929A (SHIPS) 20 August 1962

Plastic Material, Cellular Polyurethane - Rigid Foam-in-Place,
Low Density

Mil-D-43110 (MR) 5 October 1962

Plastic Foam Insulation, Thermal

HH-1-00530 (GSA-FSS) April 25, 1963

Interior Federal Specification - Insulating Board, Thermal
(Urethane)

U. S. Dept. Commerce - Spec. No. 32-MA-5b - January 3, 1964

Plastic Material, Thermal, Cellular, Rigid

Canadian Government Specification Board - 41-GP-16 - 31 July 1964

Specification for Polyurethane Rigid, Cellular

GOVERNMENT REPORTS

Shock and Vibration Attenuation

<u>Publications</u>	<u>Subject Content</u>
AD-273 400P	Theo. of Packaging Cushioning
AD-431 513P	Energy Absorption of Low Density Plastics
PB-159 832P	22 Types of Resilient materials
AD-282 380P	Resilient Polystyrene Foam -Dynamically Tested
PP-163 470P	Packaging, 3" Better than 6"
AD-270 241P	Packaging Foam-Bottomed Out on Deflection
AD-283 935P	Foam Core Propeller Blades
AD-265 900P	Urethane Foams Between Aluminum Plates
AD-295 095P	Shock Absorbing Character of U Foam
AD-603 539P	Shock Absorption of Model Tunnel Liners
AD-605 936P	Syntactic Foams
AD-601 179P	Greenland Foam Building
AD-600 654P	Greenland Foam Building Tongue & Groove Panels
AD-437 901P	Spray Plastic Resin on Air Inflated Mold Set Up on Building Foundation
AD-603 187P	Foamed Polyethylene Dielectric Cores
AD-606 107P	Adequate Housing for Electronic Equipment and Thermal Barriers
AD-259 514P	Shipboard Use of U Foam
AD-423 386P	Foamed-in-Place Army Hospital Litter Bed

<u>Publications</u>	<u>Subject Content</u>
AD-426 294P	Rigid Foam for Energy Dissipating Properties
PP-161 367P	I. Resnick Rigid Foam Manual, 85 p. \$8.10

REFERENCES

- ASTM STP 210, "Symposium on Structural Sandwich Constructions," 1956.
- ASTM STP 217, "Symposium on Thermal Insultations," 1957.
- ASTM STP 344, "Symposium on Fire Test Methods," 1963.
- ASTM Part 26 -- Plastics Specifications, 1966.
- ASTM Part 27 -- Plastics Methods of Testing, 1966
- ASTM Part 28 -- Rubber, Carbon Blacks; Gaskets, 1967.
- Harding, R. J., "Determination of Average Cell Volume of Foam Plastics", Modern Plastics, Vol. 37, p. 162, June 1960.
- Remington, W. J., and R. Pariser, "A New Apparatus for Determining the Cell Structure of Cellular Materials," Rubber World, Vol. 138, 261 (May 1958).

WAAshe/mh
3-15-67

WAA-16-67

Figure 1. Die for Stamping Tension Specimens

D-1564

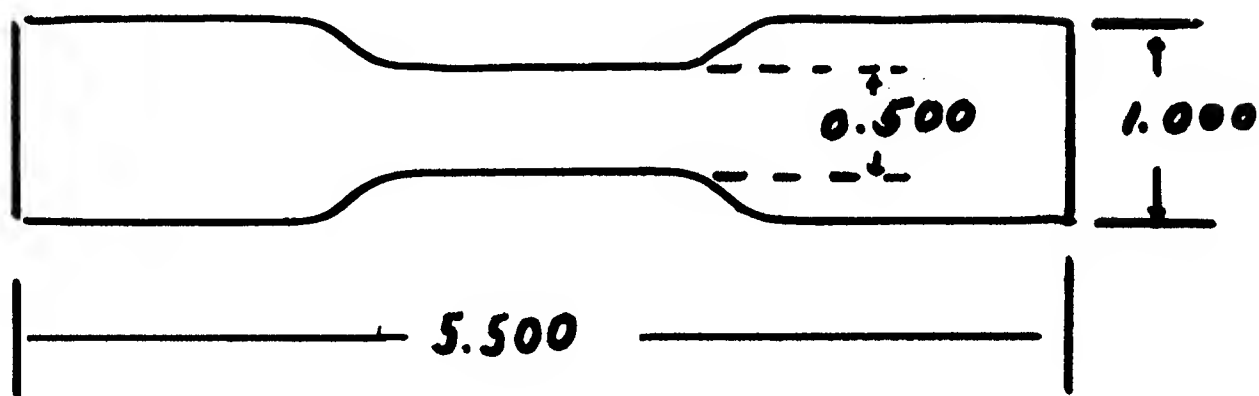


Figure 2. Block Shape Tear Specimen

D-1564

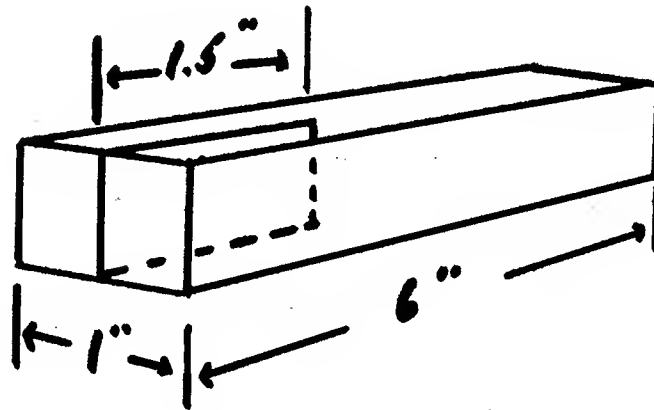


Figure 3. Graves Tear D-624

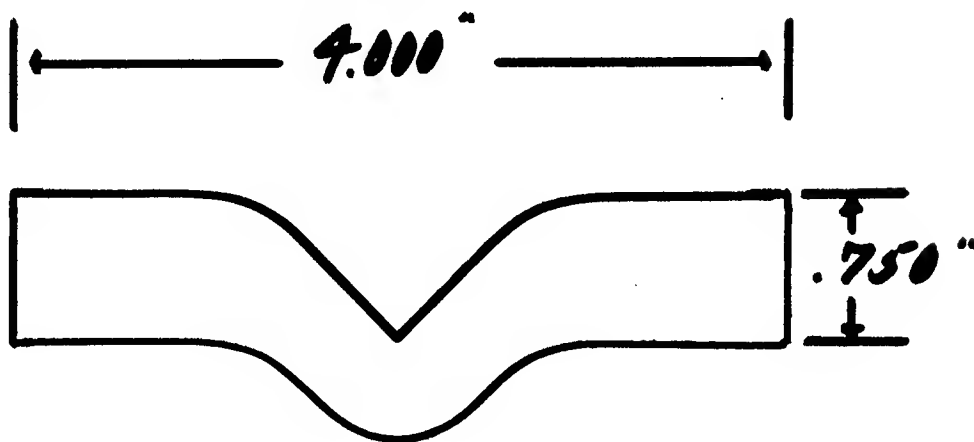


Figure 4. Trapezoid Tear

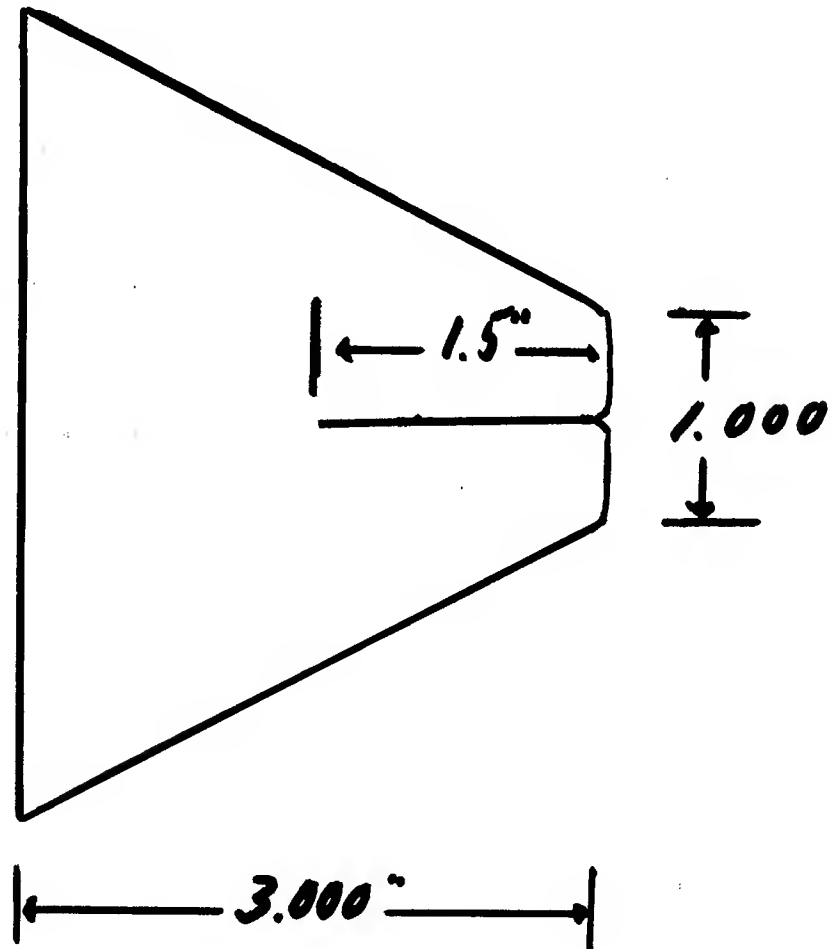
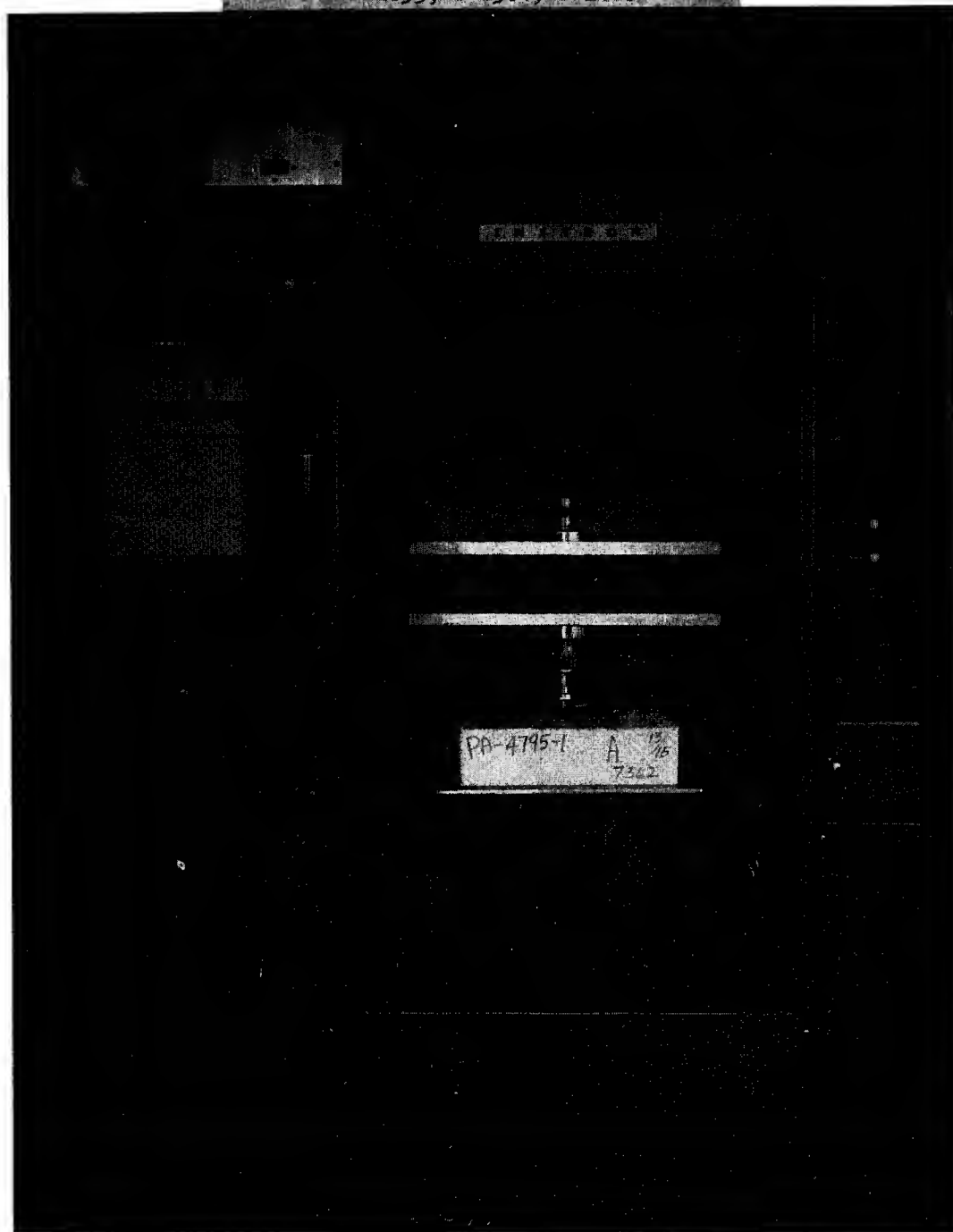


Figure 5. Instron Equipped to Run I.D.
D-1055, D-1564, D-2406



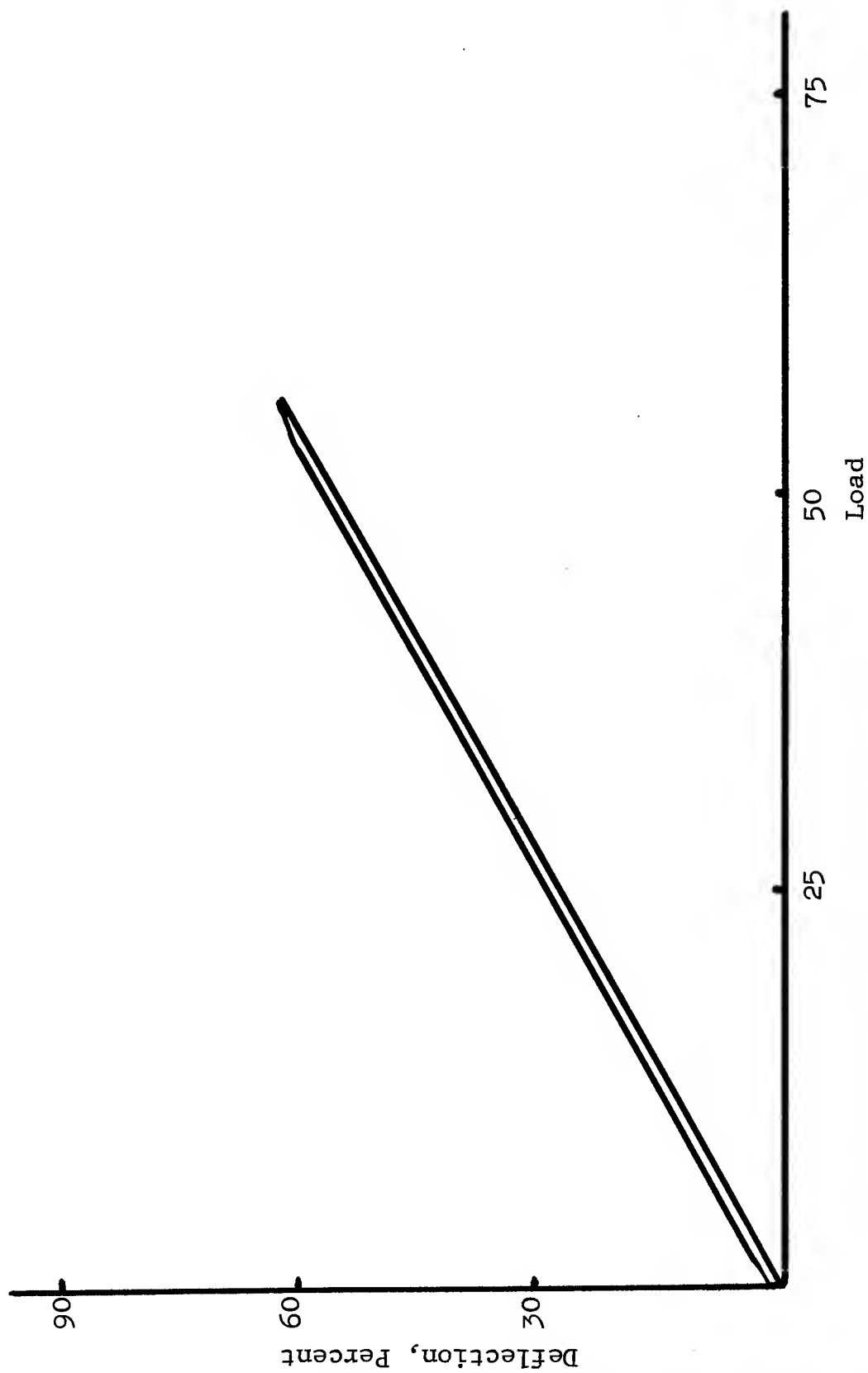


Figure 6 - 1. Load Deflection of a Coiled Steel Spring

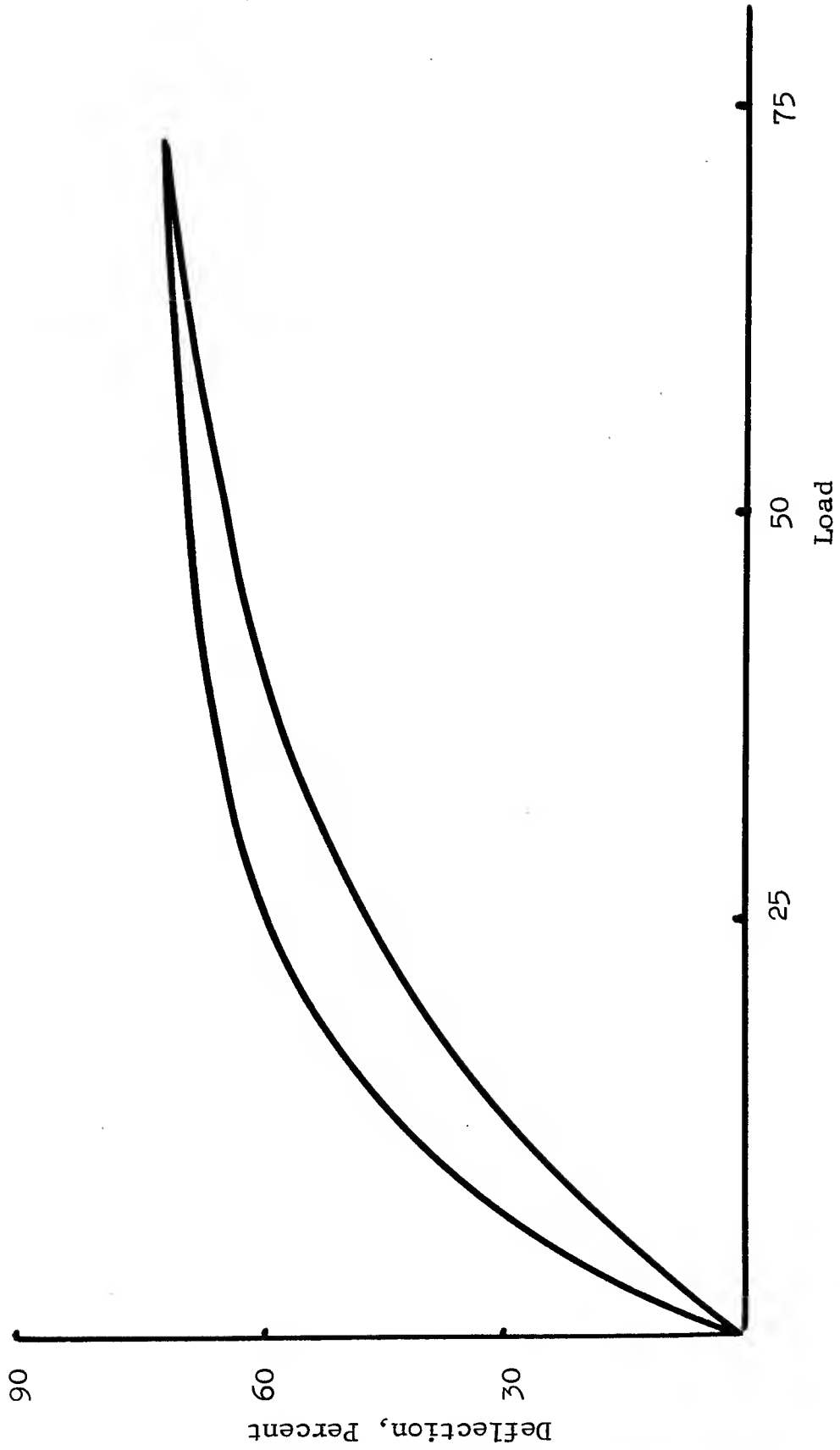


Figure 6 - 2. Load Deflection of Molded Cored Rubber

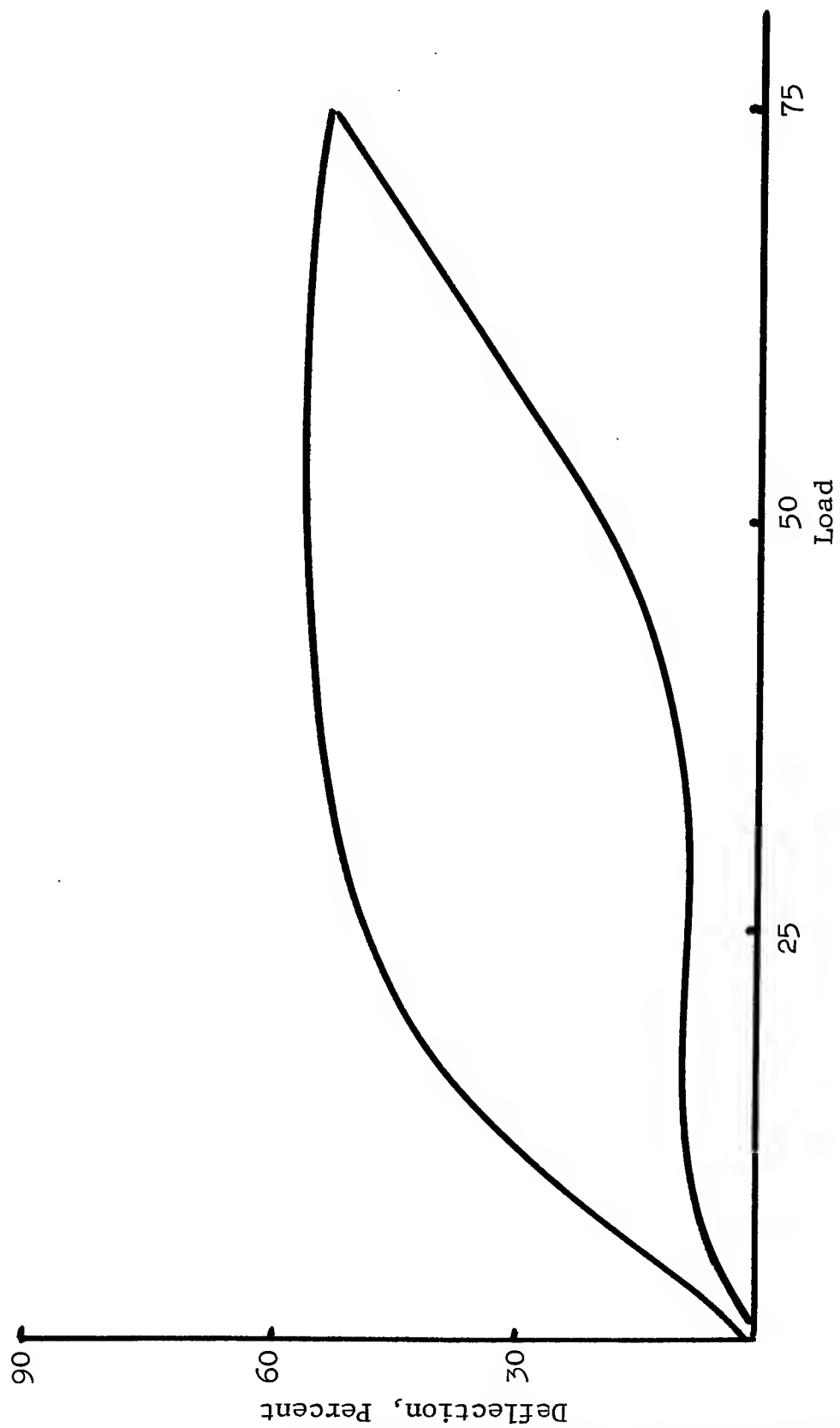


Figure 6 - 3. Load Deflection of Polyester Slab Foam

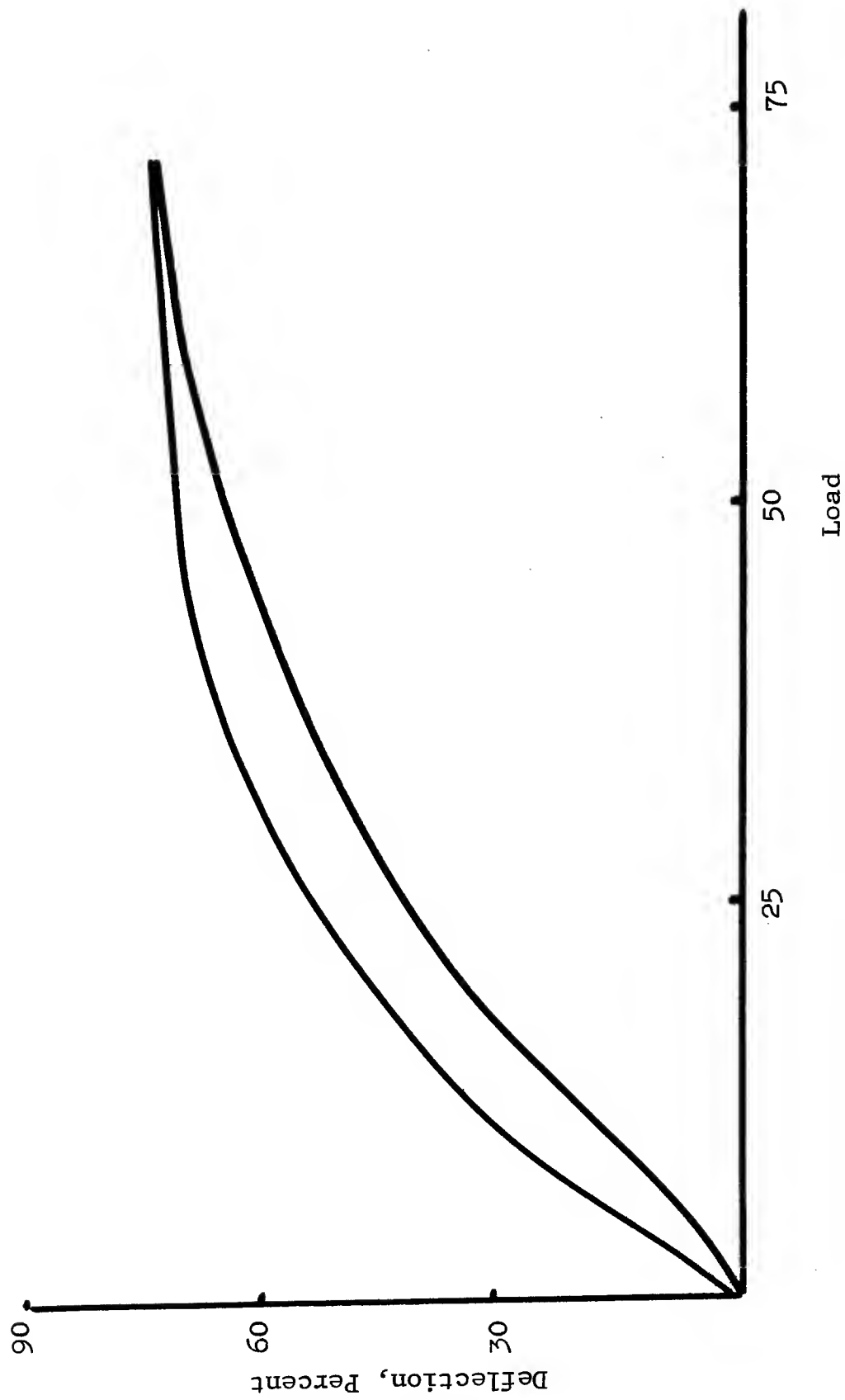


Figure 6 - 4. Load Deflection of a Polyether Molded Foam

No. 445 Urethane Foam Test Machine

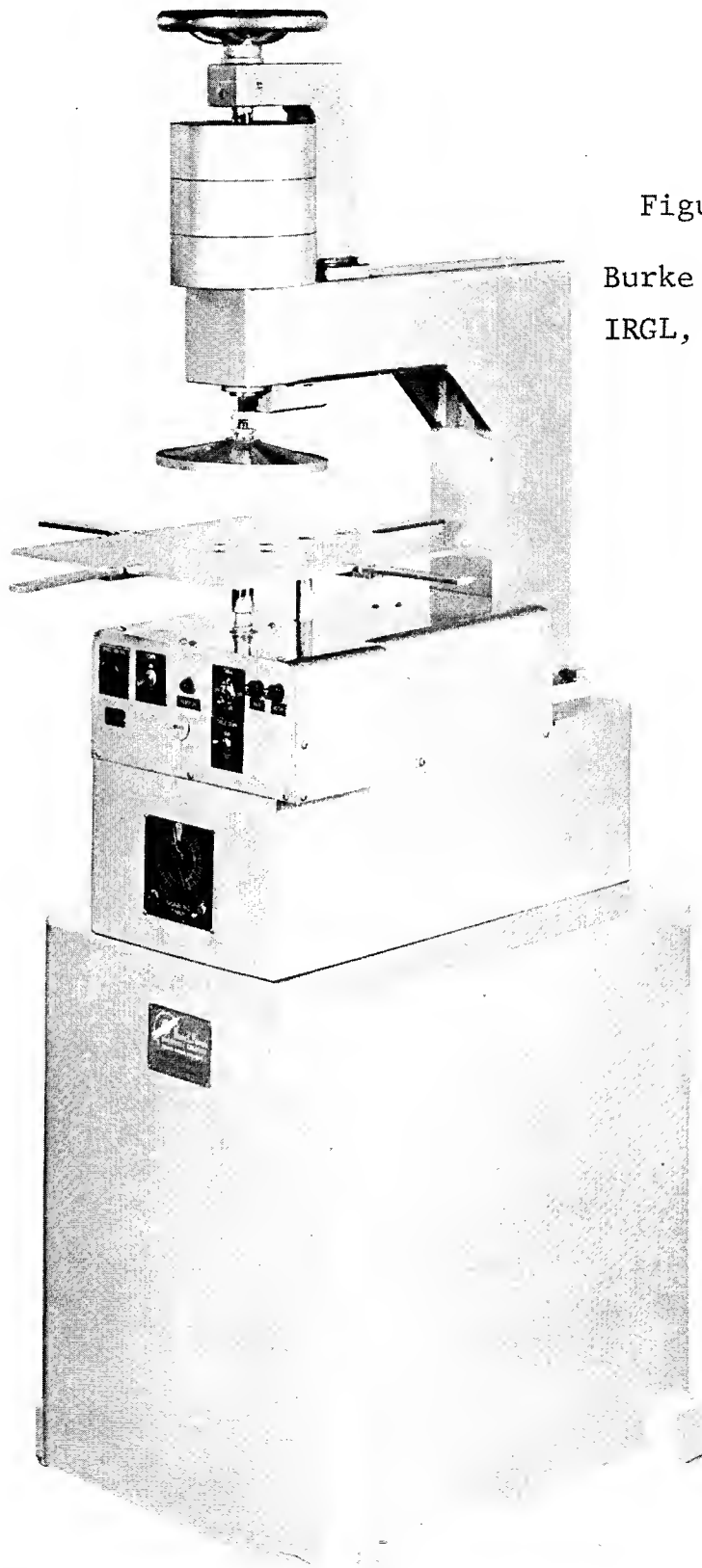


Figure 7.

Burke Porter Tester
IRGL, D-1564, D-2406

244

BURKE PORTER MACHINERY CO.
Grand Rapids, Michigan

Figure 8. Dynamic Fatigue Tester
D-1055, D-1564, D-2406

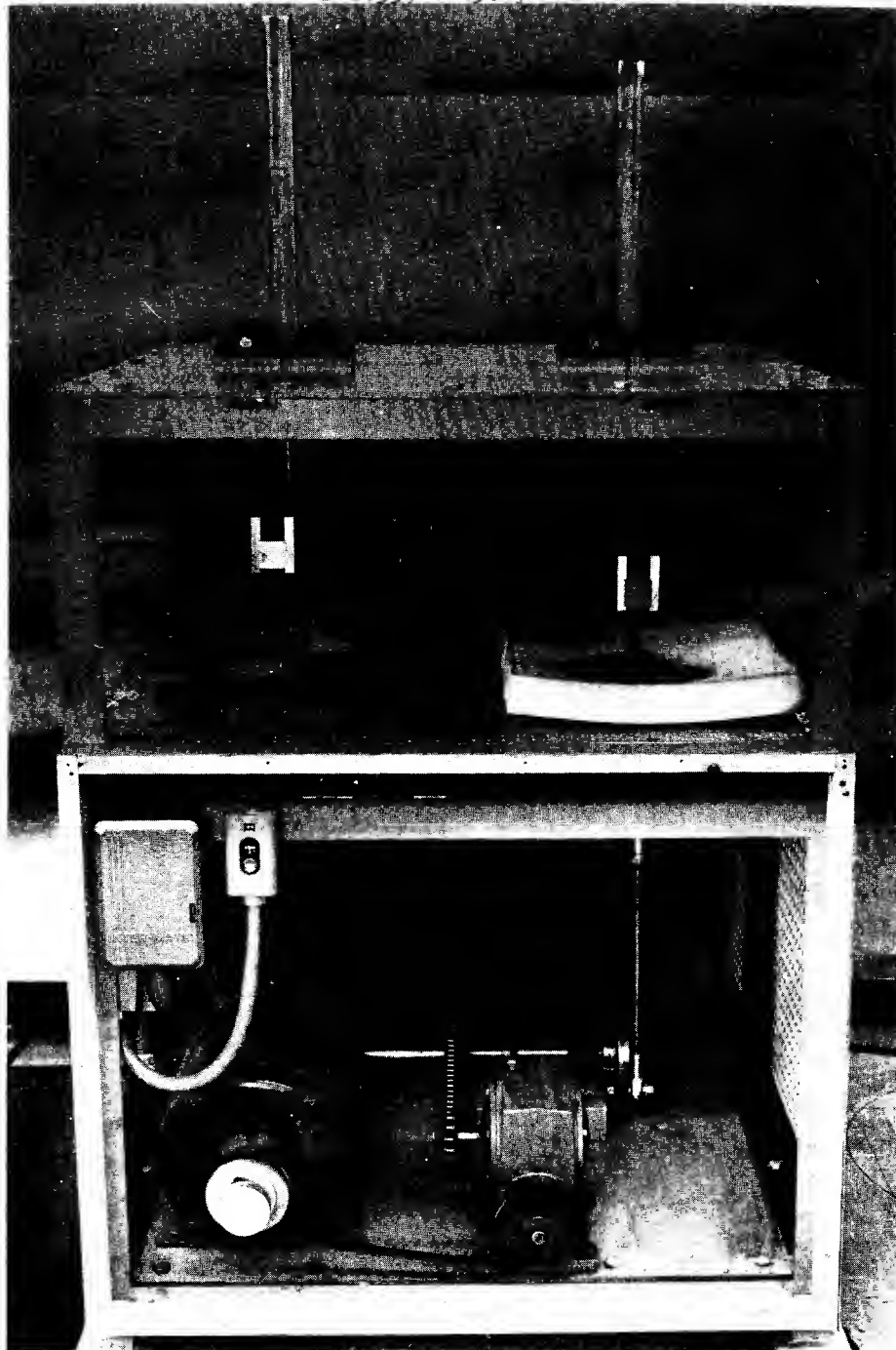
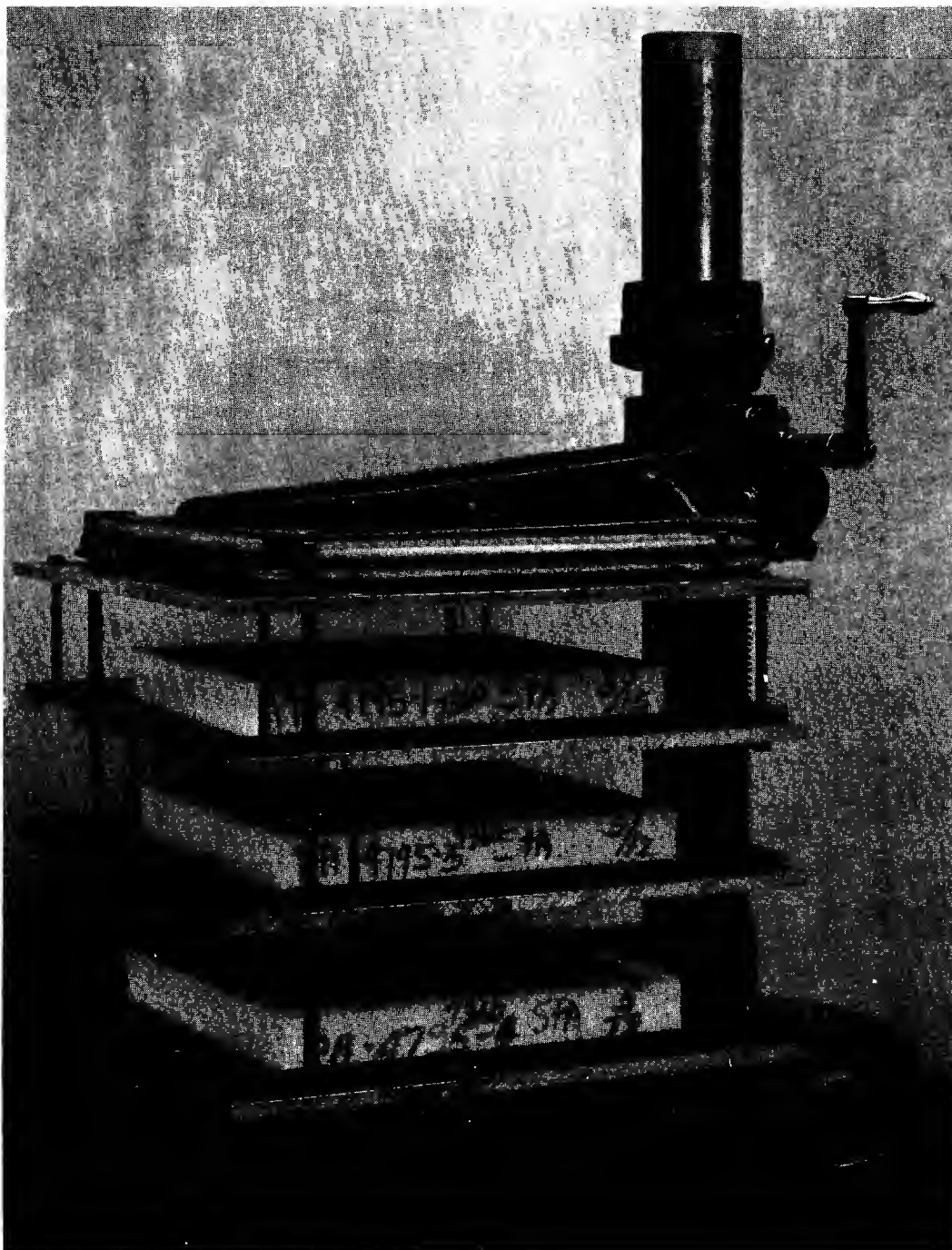


Figure 9. Static Fatigue Apparatus
D-1564, D-2406



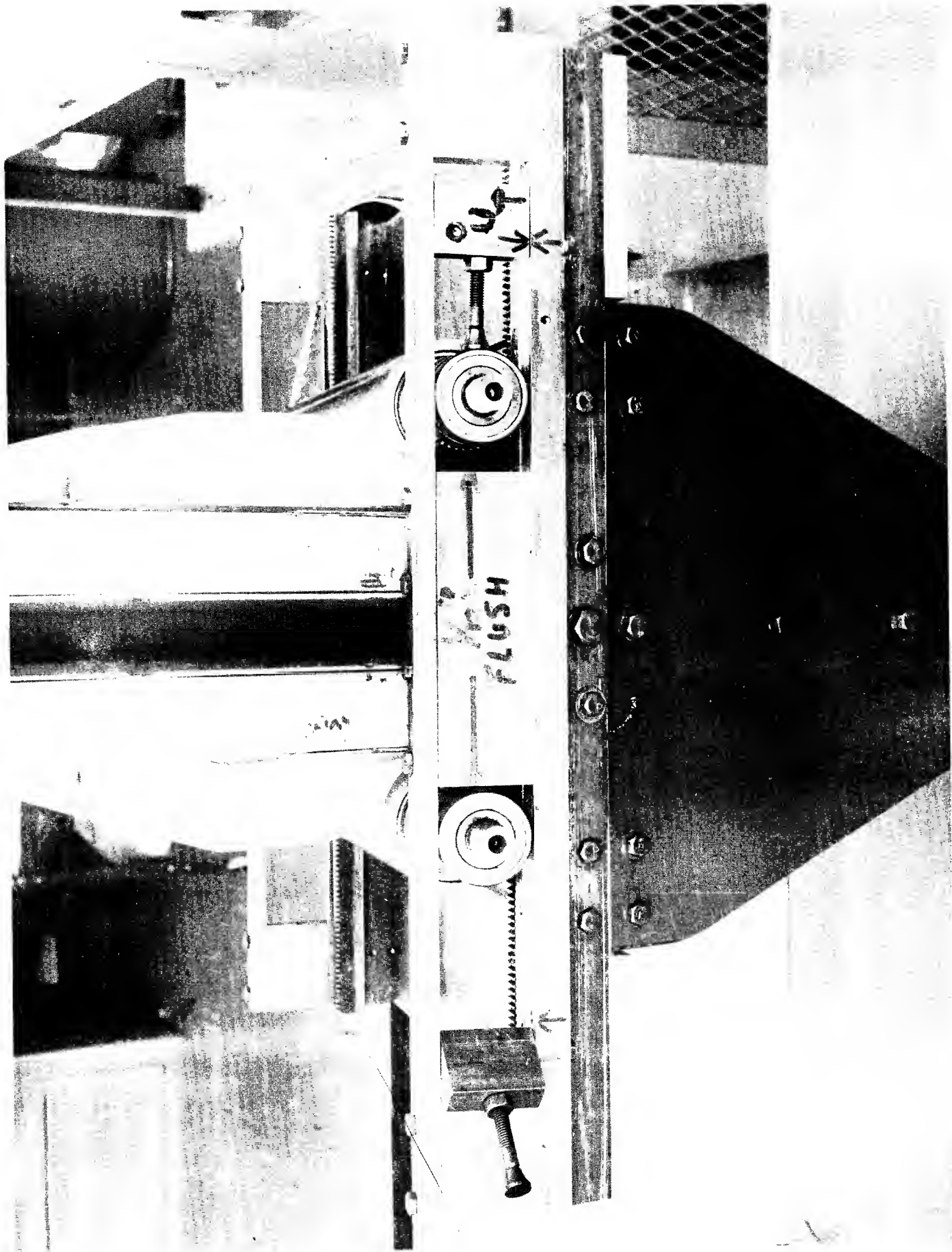


Figure 10. Roller Shear Fatigue Apparatus
D-1564, D-2406

Figure 11. Band Saw with Adjustable Box for Cutting Foam

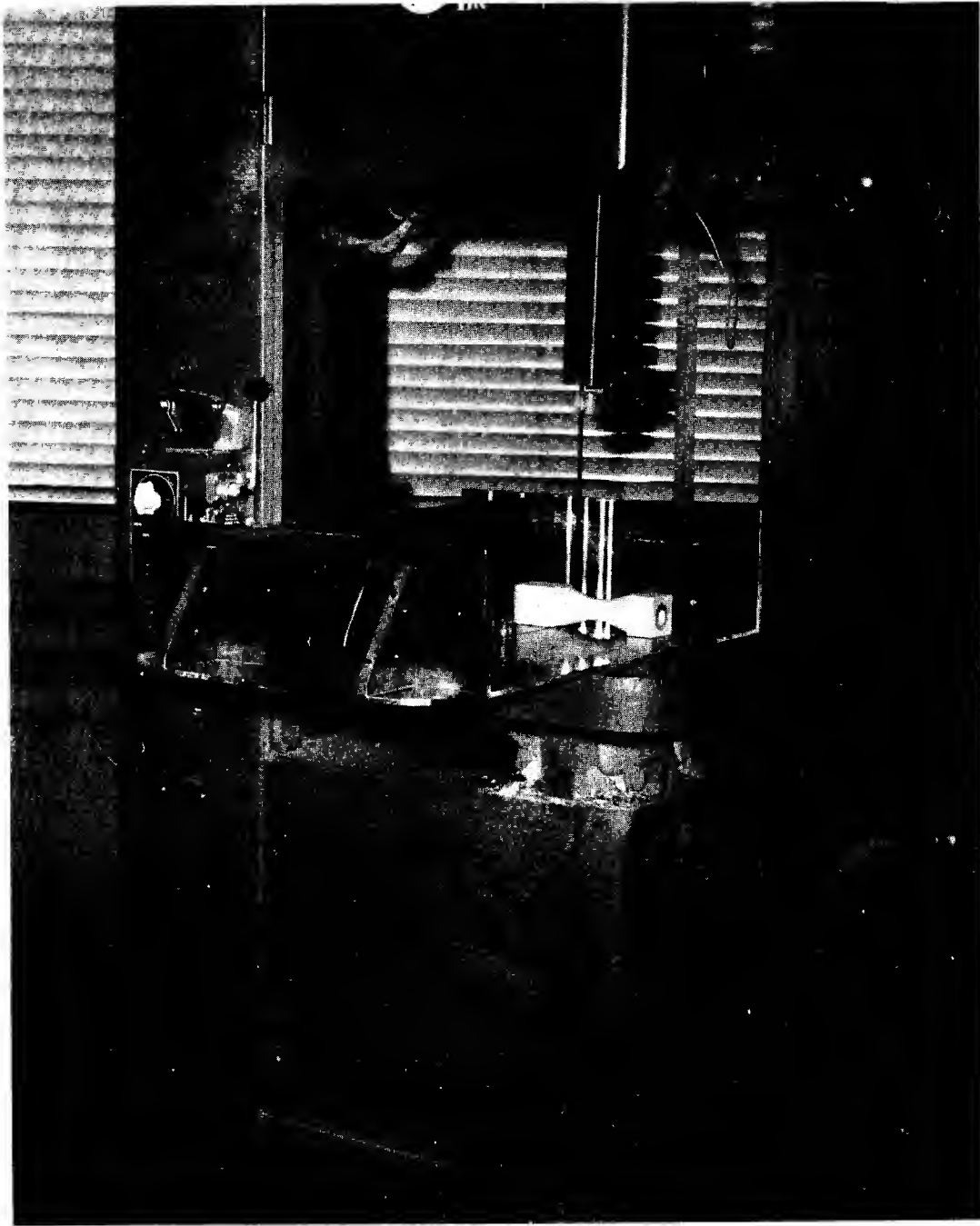
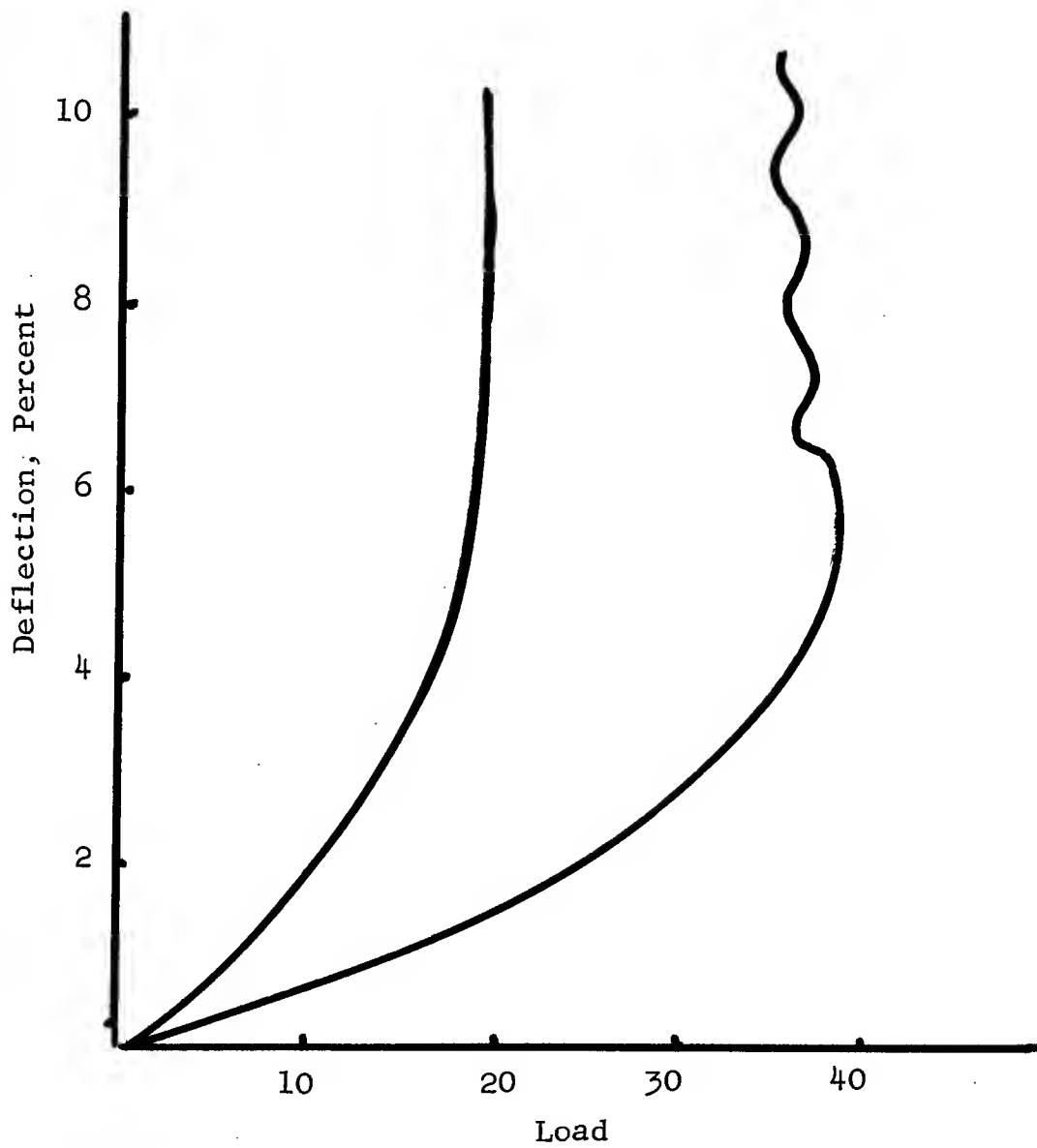


Figure 12.



Load Deflection Rigid Urethane Foam
Parallel and Perpendicular

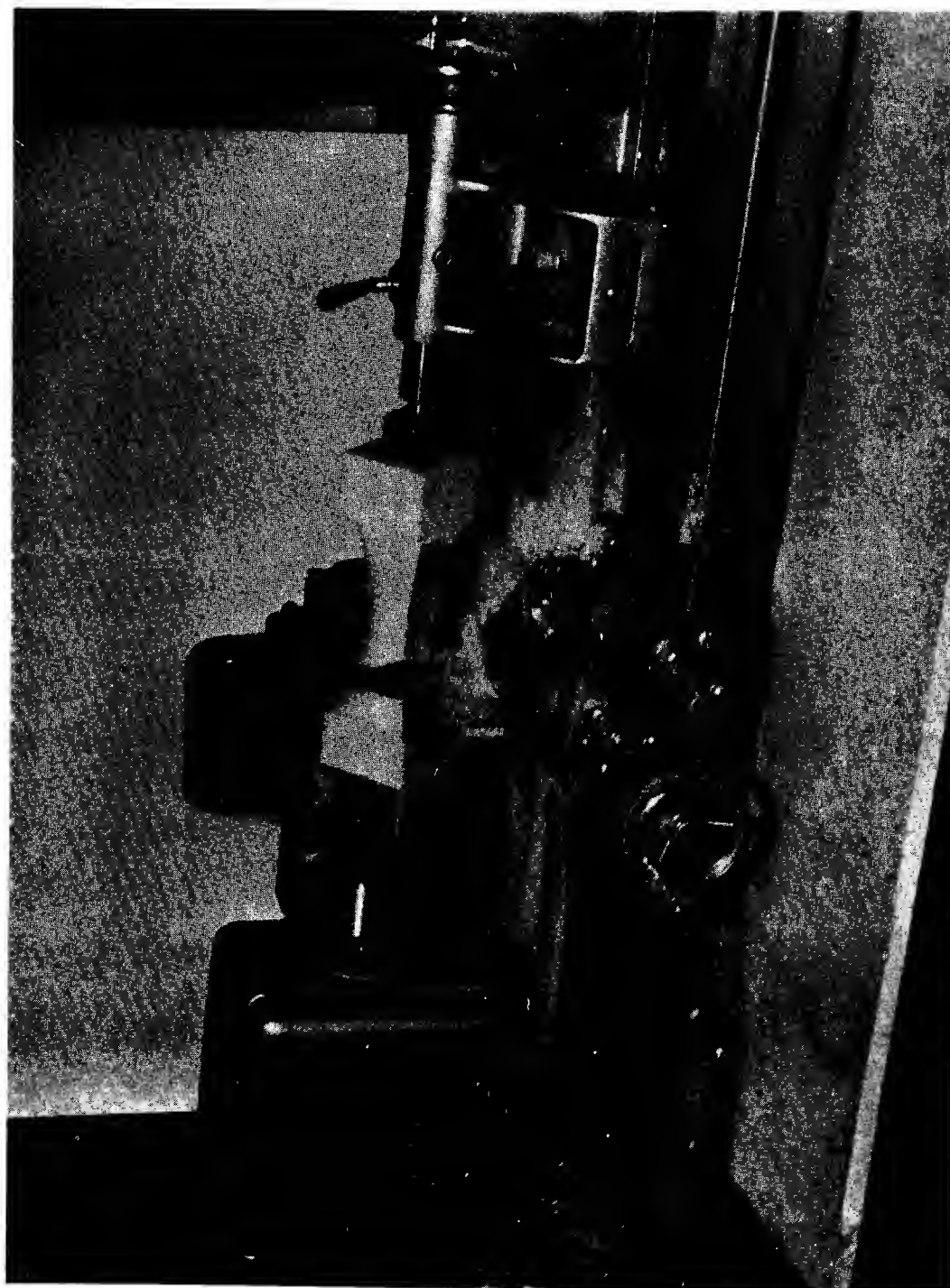


Figure 13. Lathe for Cutting Type A Rigid Tensile Specimens

Figure 14. Instron Equipped to Run Type A Rigid Tensile Specimens

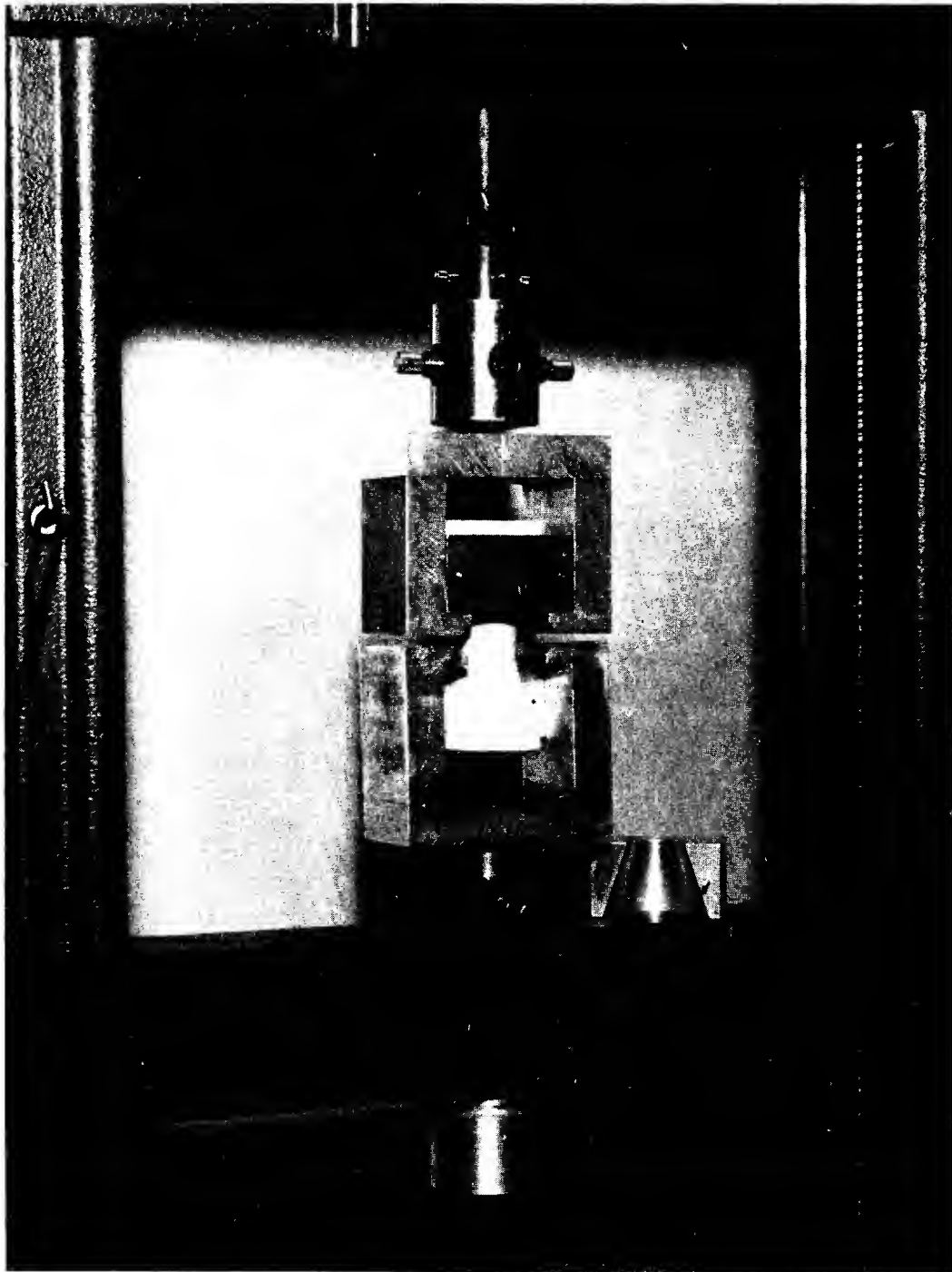
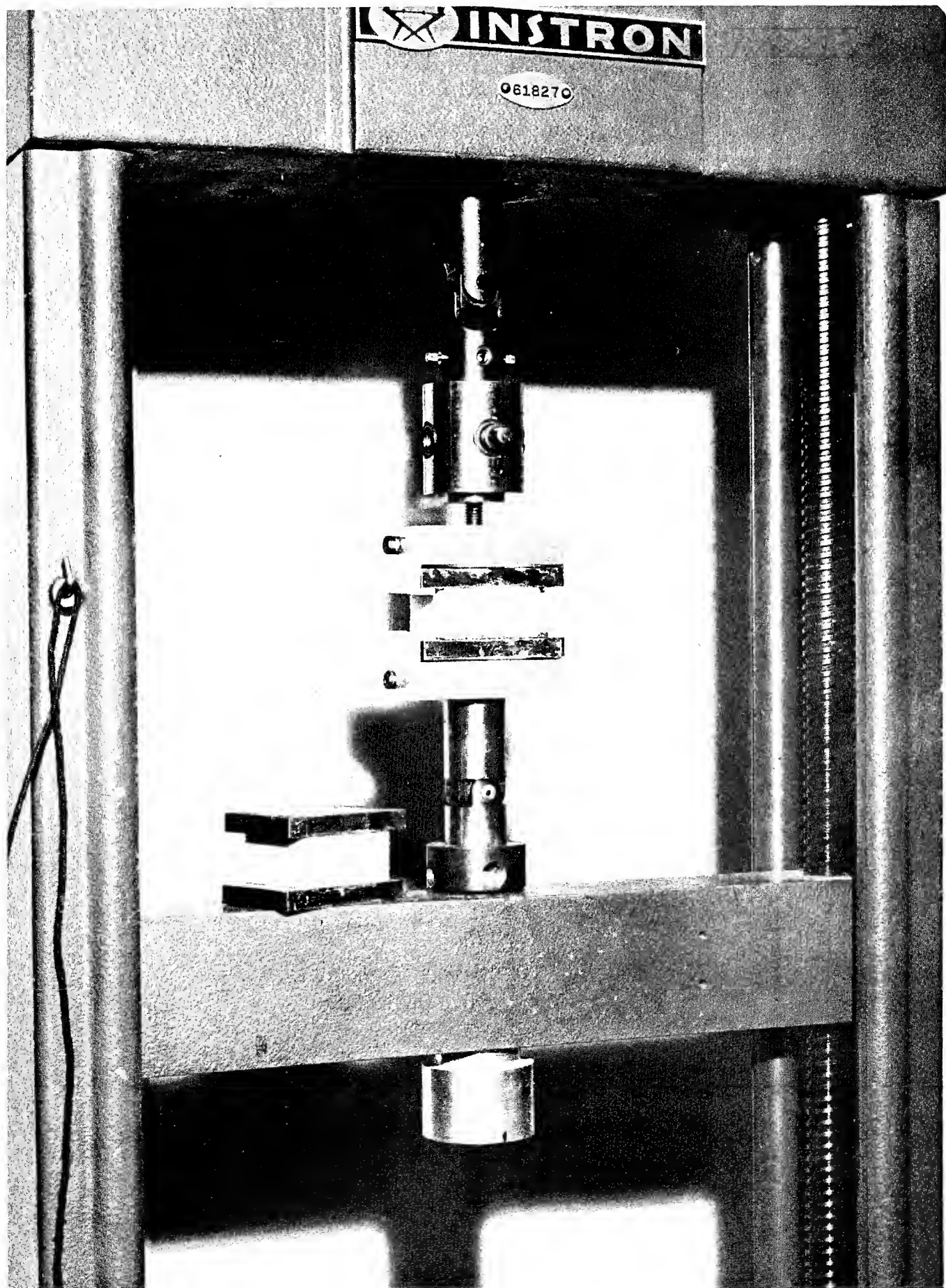


Figure 15. Instron Equipped to Run Type B Rigid Tensile Specimens



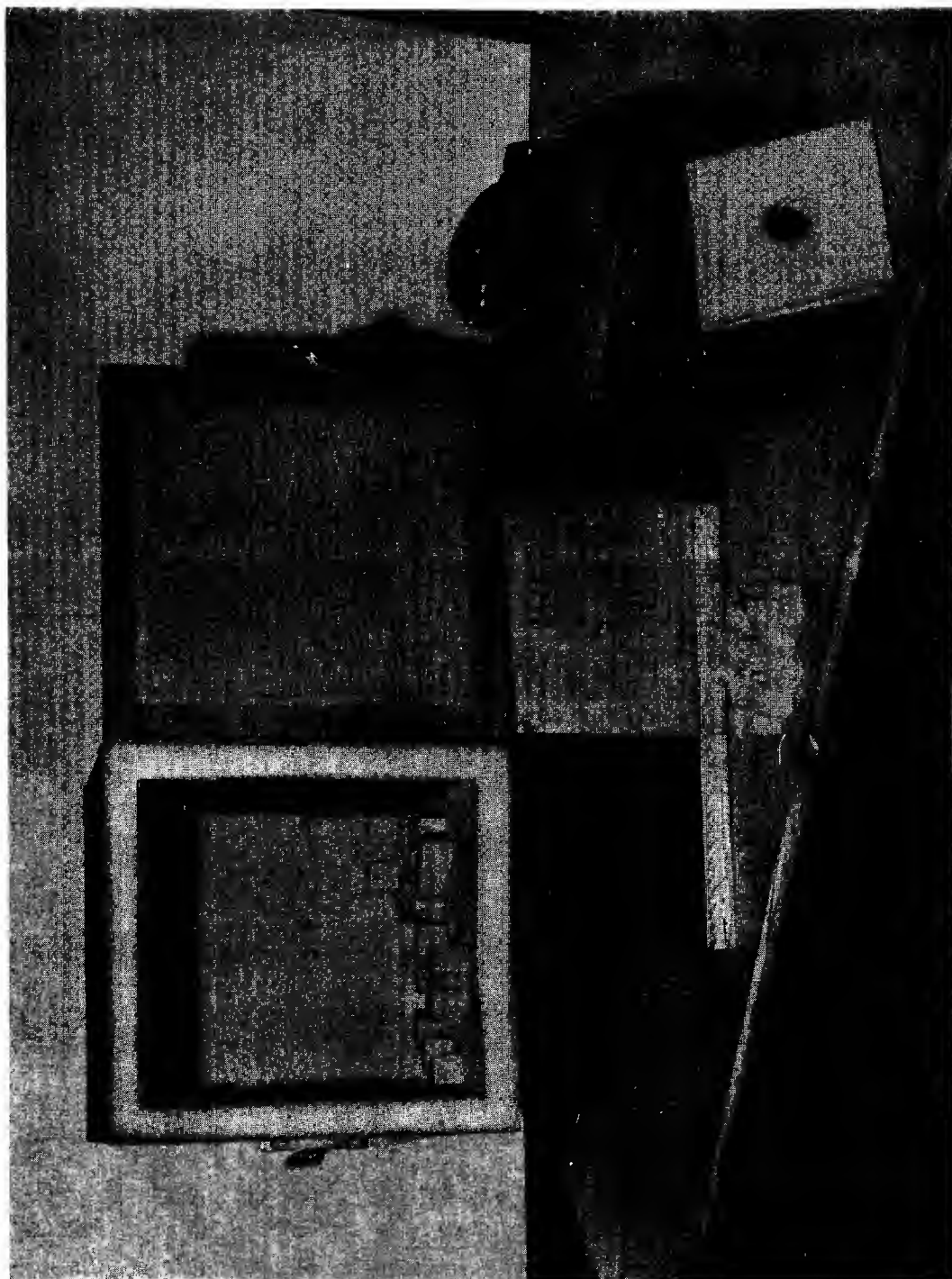


Figure 16. Friability testing.
Box for Tumbling Specimens ASTM C-421 & Taber Abraser for Flat Sheets

Figure 17. Friability Surface Tester.
Manufactured by Custom Scientific Instruments Inc.



Figure 18. Porosity Measurement
Glass Apparatus D-1940 & Beckman Air Pycnometer

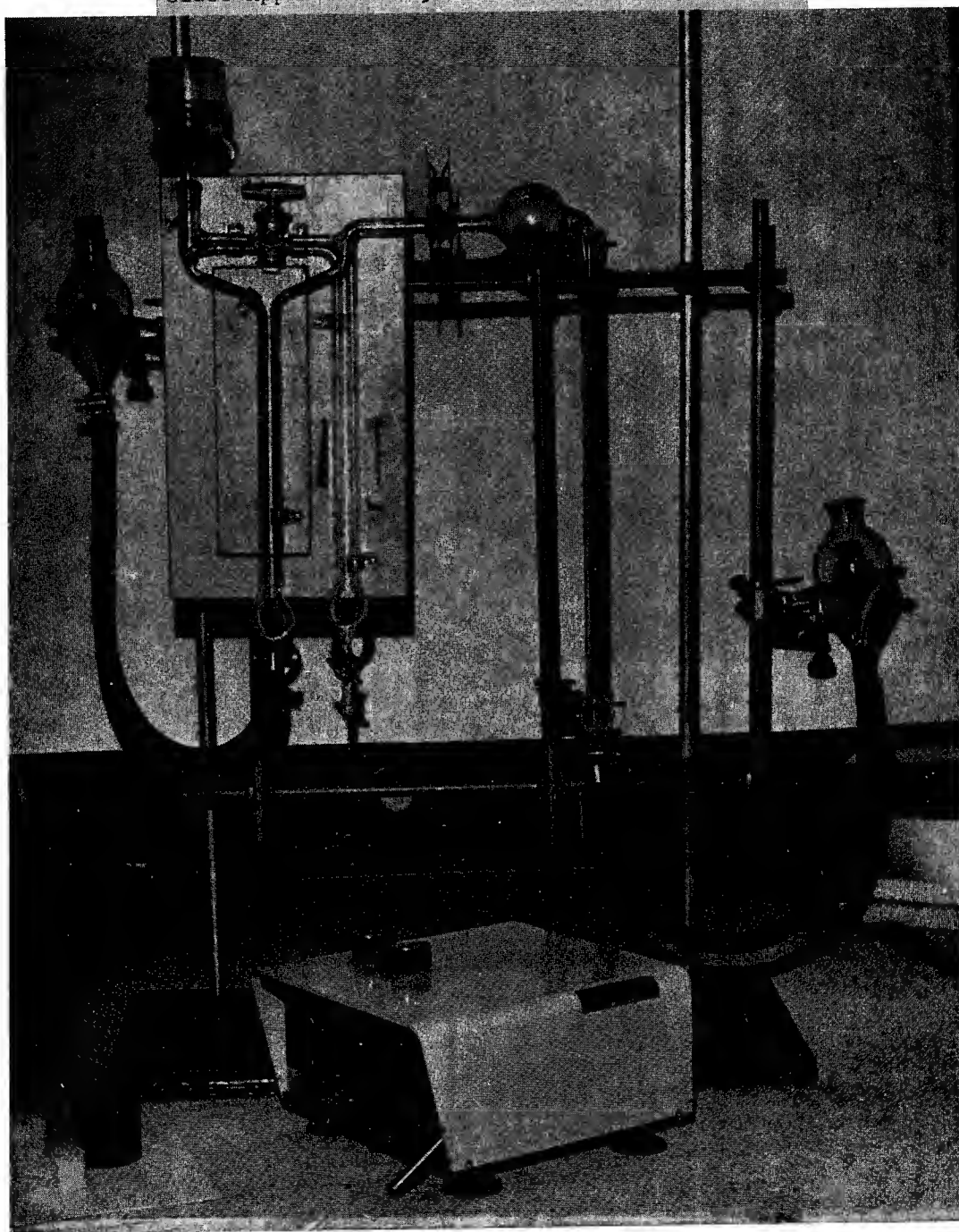


Figure 19. Instron Equipped to Run Shear Strength ASTM C-273

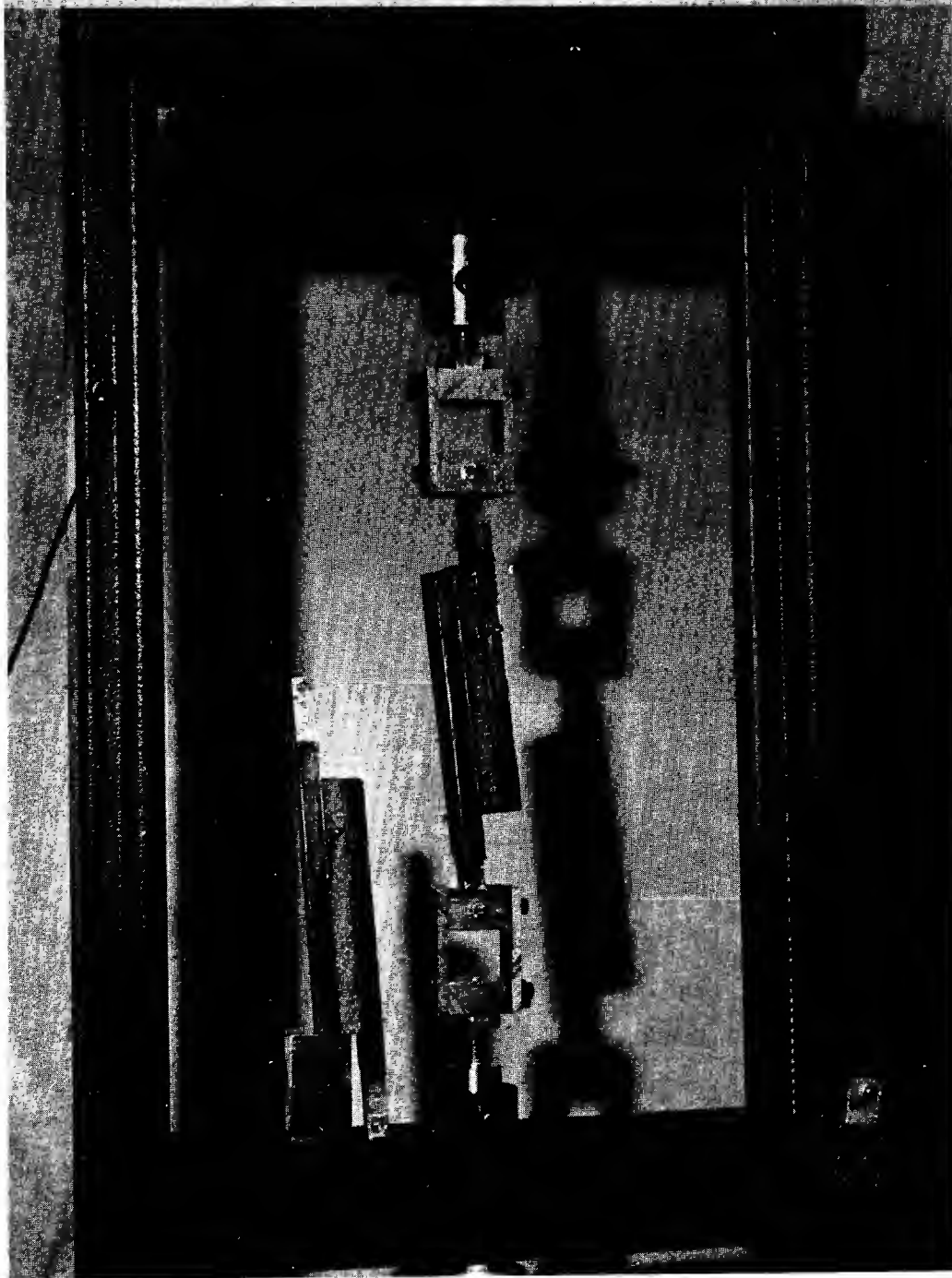
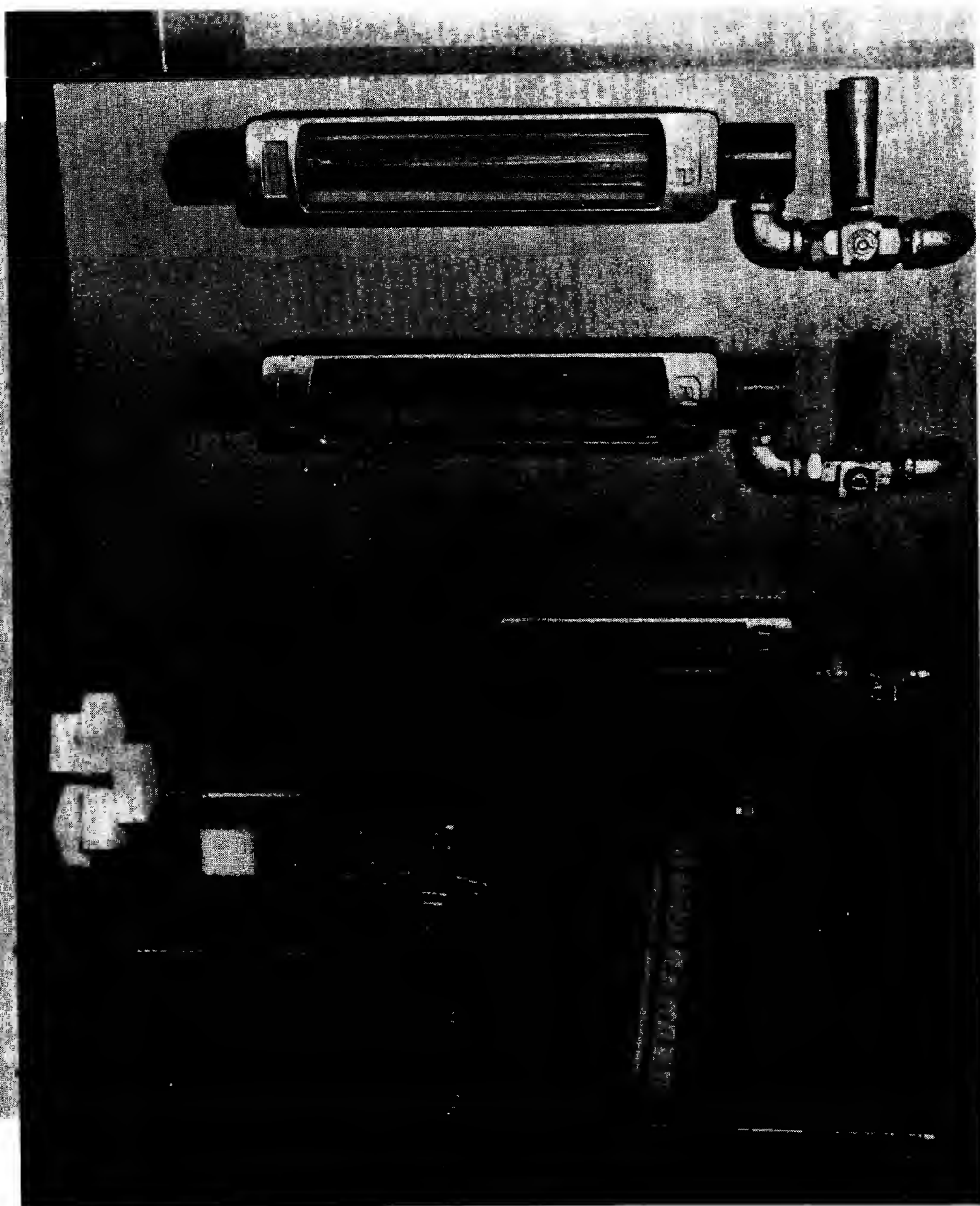


Figure 20. Instrument for measuring air flow resistance of flexible foam



CELLULAR PLASTICS TECHNOLOGY

May 1-5, 1967

ROSTER

Alvares, Edgardo J.
International Cellulose Res. Ltd.
Rayon Research Division
Hawthornbury, Ontario, Canada

Beal, Kenneth W.
Cellery Chemical Company
Cellery, Pa. 16024

Bigelow, Robert A.
Freeman Chemical
222 E. Main Street
Urethane Laboratory
Port Washington, Wisc.

Bitner, Clarence L. Jr.
Armstrong Cork Co.
R & D. Center
Lancaster, Pa.

Bryant, Robert M.
Dow Corning Corp.
Chemical Products
Midland, Michigan

Buese, George J.
Johnson & Johnson
Highway #1
New Brunswick, N. J.

Burns, Robert T.
Hercules Inc.
Engineering Department
910 Market St.
Wilmington, Delaware

Clyer, William B.
Gulf Research and
Development Company
9009 West 67th Street
Merriam, Kansas

Cardinal Earl V.
Abbott Laboratories
North Chicago, Ill

Clam, Robert B.
Redstone Arsenal
AMSMT-DELC - Bldg. 4500
Redstone Arsenal, Ala. 35809

Cyba, Henry A.
Universal Oil Products
Des Plaines, Ill.

Davies, Edward A.
Imperial Oil Enterprises Ltd.
Research Division
Box 3022
Sarnia, Ontario, Canada

Dozienspleet, Ralph E.
Monsanto Canada Ltd.
Woodbridge, Ontario, Canada

Esmay, Donald L.
3 M Company
Industrial Tape Division
2501 Hudson Road
Minneapolis, Minn.

Gooch, Hiram D.
Brulin & Company, Inc.
2920 Martindale Ave.
Indianapolis, Ind.

Haluska, Loren A.
Dow Corning Corp.
Chemical Products
Midland, Michigan

Hermanson, Ralph
Sandle Corporation
Div 2564, Box 4800
Albuquerque, N. M. 87115

Karalis, Tom J.
Witco Chemical Company
6200 W. 51 St.
Chicago, Ill. 60638

NOT AVAILABLE TO DTIC DOES NOT PERMIT FULLY REPRODUCED

Serekes, Peter S.
Building Products of Canada Ltd.
Research & Development
Box 6063
Montreal, P. Q., Canada

Giachif, M. Fred
L. J. du Pont de Nemours & Co.
Film Department
Christina Lab
Wilmington, Del. 19898

Gnutson, Robert J.
Malco Chemical
5216 W. 66th Place
Chicago, Ill. 60638

Golakowski, Richard A.
The Upjohn Company
Darwin Research Div.
110 Sackett Pt. Road
North Haven, Conn.

Gourtides, Demetrius A.
ASA-AMES Research Center
Technical Service
Loffett Field, Calif. 94035

Landrock, Arthur H.
Plastics Tech. Evaluation Cntr
Picatinny Arsenal
Building 3401
Dover, N. J. 07801

Luskin, Robert M.
Timberly-Clark Corp.
Project Leader
Greenah, Wisconsin

Lay, Vern T.
Low Chemical Company
Project Leader
Physics Lab - 555 Building
Midland, Michigan 48640

McCann, Joseph E.
Leeves Brothers
Iron Division
Box 188
Cornelius N. C. 28031

McIlroy, Henry M.
Bendix Corporation
Materials Engineer
Box 1159
Kansas City, Missouri

Nelson, Edward C.
General Motors Corp.
Fisher Body Division
Process Development Dept. #70
Warren, Michigan 48090

Novotny, John J.
Atlas Chemical Industries, Inc.
C. E. L. Division
Wilmington, Delaware

Ostfield, Howard G.
Mobay Chemical Co.
Penn Lincoln Parkway West
Pittsburgh, Pa. 15205

Pettebone, Russell H.
Merck & Co., Inc.
Chemical Div.
Product Development Service Labs
Rahway, N. J. 07065

Retford, D. T.
MacGregor Division
Brunswick Corporation
I-75 at Jimson Roads
Cincinnati, Ohio 45215

Rider, Harold D.
Marathon Oil Company
Research Center
Box 269
Littleton, Colorado

Rinde, James A.
University of California
Lawrence Radiation Lab
Box 808 - L-421
Livermore, Calif. 94550

Rosa, Daniel
Bostrom Company
133 W. Oregon St.
Milwaukee, Wisconsin

COPY AVAILABLE TO DTIC DOES NOT PRESENT FULLY LEGAL EFFECT

Roth, Gerald
Swift & Company
Chemicals for Industry
Chi Stockyards
Packer & Exchange
Chicago, Illinois

Scully, Daniel
Mallinckrodt Chemical Works
Industrial Division
3700 Broadway
St. Louis, Missouri

Sharp, John A.
Canadian Industries Ltd.
Central Research Lab
McMasterville, Quebec, Canada

Shoustal, James C.
Scott Paper Company
Research Division
Philadelphia, Pa.

Strickel, William R.
Johnson & Johnson
4949 West 65th St.
Chicago, Ill. 60638

Wiseman, Richard Scott
Scott-Wise Polymers
Crowley, Louisiana

Wiste, Orville M.
3 M Company
New Products Department
2501 Hudson Road
St. Paul, Minn.

Uhl, William J.
Koppers Company, Inc.
Koppers Building
Pittsburgh, Pa. 15219

Vermeulen, Jacob J.
Shell Chemical Company
KSPLD
P. O. Box 211
Corrance, Calif.

Yeager, Frederic W.
E. I. du Pont de Nemours & Co., Inc.
Elastomers Div.
Deepwater, N. J.

Zwolinski, Leon M.
Allied Chemical Company
Morristownship Center
Morristown, N. J.

Additional Guest Lecturer

Kadowaki, Yoshio
Furukawa Electric Company
2 chome, Futaba, Shinagawaku
Tokyo, Japan

COPY AVAILABLE TO DTIC DOES NOT PERMIT FULLY LEGIBLE REPRODUCTION

CELLULAR PLASTICS TECHNOLOGY

Guest Lecturers

William A. Ashe
Res. Section Head
Methane Application Research
Wyandotte Chemicals Corp.
1609 Biddle
Wyandotte, Michigan 48192

Dr. Calvin J. Benning
L. R. Grace & Company
Research Division
Washington Research Center
Clarksville, Maryland 21029

Edward Cuddihy
Research Engineer
Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, Calif. 91103

Carlos Hilado
Union Carbide Corporation
Chemical Division
Technical Center
Box 8361
S. Charleston, W. Va. 25303

J. J. Hoskin
Joint Managing Director
Elliott Electronic Tubes Ltd.
Elstree Way, Borehamwood
Hertfordshire, England

A. R. Ingram (Dr.)
Koppers Company, Inc.
Research Department
140 College Park Drive
Monroeville, Pa. 15146

Dr. B. Kanner
Union Carbide Silicones Div.
Sterling Forest Res. Center
P. O. Box 324
Tuxedo, New York 10987

M. Melvin Kaplan
Allied Chemical Corp.
Industrial Chemical Div.
1051 S. Park Ave.
Buffalo 5, New York

Dr. K. C. Frisch
Wyandotte Chemicals Corp.
Industrial Chemicals Group
1609 Biddle
Wyandotte, Michigan 48192

T. P. Martens
Sinclair-Koppers Company
Product Development Dept.
Monaca, Pa.

Dr. J. Moacanin
Research Group Supervisor
Jet Propulsion Laboratories
4800 Oak Grove Drive
Pasadena, Calif. 91103

Raymond L. Siren
Mobay Chemical Company
Penn Lincoln Parkway West
Pittsburgh, Pa. 15205

F. J. Wherley
Sr. Research Chemist
B. F. Goodrich Company
Research Center
Brecksville, Ohio 44141

R. J. Winne
Packaging Engineer
Westinghouse Electric Corp.
R & D Center
Beulah Road, Churchill Boro
Pittsburgh 35, Pa.

R. L. Zimmerman
The Dow Chemical Company
Plastics Development & Service
433 Building
P. O. Box 467
Midland, Michigan 48641

Prof. Irving N. Einhorn
Department of Chemical Engineering
Wayne State University
701 W. Warren
Detroit, Michigan 48202

COPY AVAILABLE TO DTIC LOGS HOW MANY TIMES THIS SPECIFIC REPRODUCTION